The Effect of Heat Treatment on Pitch Quality

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Publication date:
2001

Document Version
Publisher's PDF, also known as Version of record

The Effect of Heat Treatment on Pitch Quality

by

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Ph.D. Thesis

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ISBN 87-90142-61-6

Printed by Nørhaven Digital, Copenhagen, Denmark

Preface

This thesis is submitted to fulfill partially the requirements for the Ph.D. degree at the Technical University of Denmark. The project has been financially supported by Koppers Denmark and ATV under the Industrial Research Education Program (EF699). The work was carried out at the Department of Chemical Engineering, DTU, in the Koppers Denmark laboratory and in the Technical Center of Koppers Industries, Harmarville, USA.

Simon Ivar Andersen and Erling Stenby from DTU supervised the project. On behalf of Koppers Europe the project was supervised by Olof Malmros and Nigel Turner. I would like to thank all four of them for their support and for their fruitful discussions and help during the project.

I would like to send my special thanks to everyone at the Koppers Denmark laboratory. They did a huge job of analyzing pitches and their help during the manufacture of anode pitch was crucial to the success of the project.

Everybody at the Harmarville Technical Center helped make my stay in Pennsylvania unforgettable. The efforts of Tom Baron, Tom Mutschler, Eric, Greg and Patrick during the manufacture and testing of anodes and of Bob Wombles, Kathy and Ken during practical arrangements are gratefully acknowledged.

The project got some extra help from people not directly connected with it. Rachel Carlson did a great job of helping with the GC and GC-MS analyses of tar oils as well as being a really good friend. Ralph Gray made an extra effort as regards the analysis of pitch and anodes and was able to explain the field of petrography in a very educational fashion. Moreover the thin sections would never have been prepared if it had not been for the work performed by Ruddi Perriard.

Lastly, it was always a source great pleasure and inspiration to work with the colleagues and students from IVC-SEP.

Lyngby, January 5, 2001

Birgit Elkjær Hansen

Summary

The aim of the present work has been to study binder pitch for aluminum smelting anodes. The project was carried out under the industrial Ph.D. program as a collaboration between the industrial pitch producer Koppers Denmark, the research center IVC-SEP (Department of Chemical Engineering, the Technical University of Denmark) and ATV (the Danish Academy of the Technical Sciences). The main objective of this project has been to investigate the effect of a mild thermal treatment in the production of binder pitch. The study has included the manufacturing of a large array of experimental pitch types. Pitches have been analyzed by conventional methods as well as some of a more scientific nature. Additionally, a study of bench-scale aluminum smelting anodes has been conducted in order to evaluate the pitches in a close to realistic context.

Initial experiments were made in order to establish the impact of treatment temperature and duration in the production of pitch from a petroleum precursor. The most volatile components were removed from a petroleum tar by vacuum distillation and the product was treated under N_2 pressure at varying temperatures and durations. The typical treatment lasted for six hours with temperatures ranging from 307°C to 415°C. Additional experiments were carried out at 360°C with different soak times. The treated materials were vacuum-distilled into 120°C softening point pitches. The experiments showed that it was possible to increase the toluene insoluble fraction and the coking value of the resultant pitch by carrying out a controlled thermal treatment of the precursor material. It was found that treatments at temperatures below and at 385°C did not cause mesophase formation in the resultant pitches. By thermal treatment at 360°C, the first two hours had the largest impact on the resultant pitch.

Traditionally, coal tar pitch is used as binder pitch for aluminum smelting anodes. The influence of the precursor origin was tested by producing pitch from both petroleum tar and coal tar. The two pure feedstocks and mixtures of them were heat-treated for six hours at four temperatures: 350°C, 370°C, 385°C and 410°C, and the heat-treated samples were distilled into pitch. It was found that the petroleum material was more sensitive to the

treatment than coal tar material and that there was no significant interaction between the two materials in the measured temperature range.

The pitches were submitted to analytical tests, especially aimed at the heaviest components in the materials. It was found that it was possible to obtain information about the formation of the heaviest components in the pitch by analyzing the toluene insoluble fraction by size exclusion chromatography with NMP as mobile phase. The method made it possible to detect formation of heavy (or more specifically early eluted) components. The concentration of these components increased with increasing treatment temperature. When mesophase appeared in the resultant pitches the concentration of some larger components was reduced in the NMP soluble part of the pitch.

Bench-scale aluminum smelting anodes were produced from experimentally produced pitches. Pitches were produced by direct distillation and by an experimental procedure inspired by the previous experiments. By optical microscopy it was found that pitches produced by a thermal treatment at 385°C followed by distillation bore traces of the thermal treatment even though limited amounts of mesophase were found.

The anodes were subjected to a comprehensive evaluation test scheme in order to establish whether the experiment binders critically influenced the anode quality. It was found that the best anode quality was produced from directly distilled coal tar pitch. Pitches containing 20% petroleum-derived material, however, showed a comparable anode performance. The experimental production method which included thermal treatment of the precursor material did not improve the anode quality compared to materials produced by straight distillation. The anodes produced from petroleum material had generally worse analytical properties than anodes produced from the other binder pitches. Thermal treatment was found to improve the performance of this particular material.

Based on the work conducted in this project it cannot be recommended to include thermal treatment procedures in the manufacture of coal tar pitch. If pitches of petroleum origin should be introduced a controlled thermal treatment would, however, be beneficial. Dual origin pitches seem to have a potential for developing new binder pitches.

Resumé

Målet med dette projekt har været at studere beg produceret til fremstilling af anoder, som anvendes til aluminiumsfremstilling. Projektet blev gennemført som et samarbejde mellem virksomheden Koppers Denmark, Center for Faseligevægte og Separationsprocesser (IVC-SEP) ved Institut for Kemiteknik, DTU, og ATV (Akademiet for de Tekniske Videnskaber). Det egentlige mål med projektet har været at undersøge virkningen af en mild varmebehandling i produktionen af beg. Dette studie har omfattet fremstilling af en lang række eksperimentelle begtyper. Disse materialer er blevet analyseret dels ved anvendelse af konventionelle metoder og dels ved anvendelse af mere videnskabeligt rettede metoder. Derudover blev der fremstillet anoder i teststørrelse for at undersøge, hvordan de eksperimentelle produkter opførte sig i en situation, der imiterede den industrielle anvendelse.

Betydningen af behandlingstid og -temperatur blev undersøgt i fremstillingen af beg fra et petroleumstjæreprodukt. Den mest flygtige del af begen blev først fjernet ved simpel destillation, hvorefter begen blev termisk behandlet under nitrogentryk. Den typiske behandling varede seks timer ved temperaturer mellem 307° og 415°C. Derudover blev der udført en måleserie med varierende behandlingstid ved en konstant temperatur på 360°C. Som et sidste produktionstrin blev materialet destilleret for at opnå beg med et smeltepunkt på 120°C. Det var muligt at forøge den endelige begs koksrest samt den fraktion af begen, der var uopløselig i toluen ved en kontrolleret varmebehandling af udgangsmaterialet. Ved temperaturer på 385°C og derunder var det muligt at undgå at danne en væskekrystallinsk mesofase i begen. Ved behandlinger ved 360°C havde de første to timer langt den største indflydelse på resultatet.

Stenkulstjærebeg er det produkt, der traditionelt anvendes ved fremstilling af anode til aluminiumsproduktion. Betydningen af tjærekilden blev undersøgt ved at fremstille beg fra både stenkulstjære og petroleumstjære. De to rene produkter samt blandinger af dem blev varmebehandlet ved fire temperaturer (350°C, 370°C, 385°C og 410°C), og de behandlede prøver blev destilleret til beg. Petroleumsproduktet viste sig at have en højere følsomhed

over for behandlingen end stenkulstjæreproduktet. Ved de anvendte temperaturer blev der ikke fundet nogen vekselvirkning mellem de to materialer.

Beg blev testet med forskellige analytiske metoder specielt rettet mod de tungeste komponenter. Størrelseskromatografi, med NMP som mobilfase, af den toluenuopløselige fraktion viste sig at være et godt værktøj til analyse af de tungeste elementer i beg. Det var muligt at følge dannelsen af tunge komponenter (eller rettere tidligt elueret) som et resultat af varmebehandling. Ved dannelsen af væskekrystal i begen faldt koncentrationen af visse af de større komponenter i den NMP-opløselige del af begen.

Der blev fremstillet testanoder i laboratorieskala ud fra eksperimentelt fremstillet beg. Beg blev dels fremstillet ved direkte destillation og ved en eksperimentel procedure, der var inspireret af de tidligere forsøg. Ved mikroskopi af begen blev det fundet, at de materialer, der var fremstillet ved en varmebehandling på 385°C opfulgt af destillation, bar præg af termisk behandling. Der blev dog ikke fundet større mængder af væskekrystallinsk fase i prøverne.

De fremstillede anoder blev undersægt i en lang række analyser. Den bedste anodekvalitet blev opnået ved brug af en stenkulstjærebeg fremstillet ved direkte destillation. Beg, der indeholdt 20% petroleumsmateriale, viste sig dog at give anoder med en sammenlignelig kvalitet. Den eksperimentelle produktionsmetode, der inkluderede varmebehandling, forbedrede ikke anodekvaliteten. Anoder produceret af petroleumsbeg viste sig at være af ringe kvalitet. Det var dog muligt at forbedre resultatet ved varmebehandling.

Baseret på de resultater der er opnået i løbet af dette projekt, kan det ikke anbefales at indføre varmebehandling i forbindelse med fremstilling af stenkulstjærebeg. Hvis beg skal fremstilles ud fra petroleumsprodukter, kan en kontrolleret varmebehandlingsprocedure med fordel indføres. Beg fremstillet af både petroleums- og stenkulstjære synes at have et stort potentiale.

List of Contents

1. Introduction

The aim of the present work has been to study binder pitch for aluminum smelting anodes. The project was carried out under the industrial Ph.D. program as a cooperation of the industrial pitch producer Koppers Denmark, the university center IVC-SEP (Department of Chemical Engineering, the Technical University of Denmark) and ATV (the Danish Academy of Technical Sciences). The commercial objective of the project has been to investigate an experimental pitch production method including a thermal treatment which would yield a better product. The scientific objective has been to investigate the chemical processes which take place during the thermal treatment process. The experiments conducted in order to achieve this objective are described in Chapters 2 to 6. The present chapter is built upon a literature study and aims at providing the reader with a basic understanding of pitch chemistry, background knowledge of the origin of the materials and the processes in which the products are used commercially. Additional literature reviews are given in the Chapter dealing with the subjects mentioned.

1.1. Pitch Chemistry

In the following section it will be attempted to give an overview of the chemical and the physical nature of pitch, aimed at readers with little or no prior knowledge of the material. The definition of pitch is wide. In this work, the word pitch characterizes a highly viscous, heavy fraction obtained from distillation of a tar. Pitch appears as a black or brownish glassy material at room temperature. When heated the pitch melts into a tar like liquid. Being a glass, the material does not have a specific melting point and it will gradually soften at temperatures between 80-130°C depending on the pitch composition.

Some pitch types, especially high-temperature coal tar pitches, contain solid particles. Quinoline is a powerful organic solvent which is capable of dissolving the majority of the pitch components and the solid particles are therefore referred to as QI (quinoline insoluble). They partly derive from small coal particles, but the majority is formed by carbonization in the coke ovens (Section 1.2.1.3). These particles have a structure and

appearance similar to carbon black. The liquid phase of a non-thermally treated pitch appears as a non-ordered liquid or isotropic phase. If the pitch is kept at temperatures above 400°C for an extended period a nematic liquid crystal phase called mesophase will appear (Brooks et al., 1965). The solid particles and the mesophase are further described in Chapter 4.

The organic origin of pitch has resulted in a content of a broad array of aromatic chemical components. It is unlikely that anyone will ever actually be able to give a full characterization of a pitch but the following types of components have been identified in pitches (Zander, 1987):

- fPolycyclic aromatic hydrocarbons (PAH)
- Alkylated PAH
- PAH with cyclopenteno moieties (acenaphthylenes)
- Partially hydrogenated PAH
- Heterosubstituted PAH: NH_2, OH
- Carbonyl derivates of PAH (Figure 1-2)
- Polycyclic heteroaromatic compounds (benzologs of pyrrole, furan, thiophene, pyridine, see Figure 1-3)

The main molecular entity in pitch is the polyaromatic hydrocarbon (PAH) skeleton. Figure 1-1 shows examples of PAH which have been identified in pitch (Blanco et al., 1991). Not all of the pitch molecules are built of a perfect structure of six atomic rings, some of the components also contain five atomic rings, like fluoranthene and acenaphthylene. Some of the pitch molecules will be substituted by alkyl and amine side chains and they can contain hydroxy groups (see Figure 1-2). Heteroaromatic rings are included in some the PAH components. In the pitch, heteroaromatic rings are part of a larger aromatic structure but the simplest possible form is shown in Figure 1-3.

It is possible to identify the lightest of the pitch components, but the maximum molecular size of the pitch components cannot be safely detected. The average molecular weights of 2500 g/mole have been detected for heavy fractions of pitch (Boenigk et al., 1990). The determination of the molecular weight of these very heavy components is complicated by

difficulties distinguishing between actual chemical bonds and associations of large molecular species. Investigations indicate that the larger components are built similarly to the lighter components and that the inclusion of heteroatoms is evenly distributed over the molecular weight (Zander, 1991).

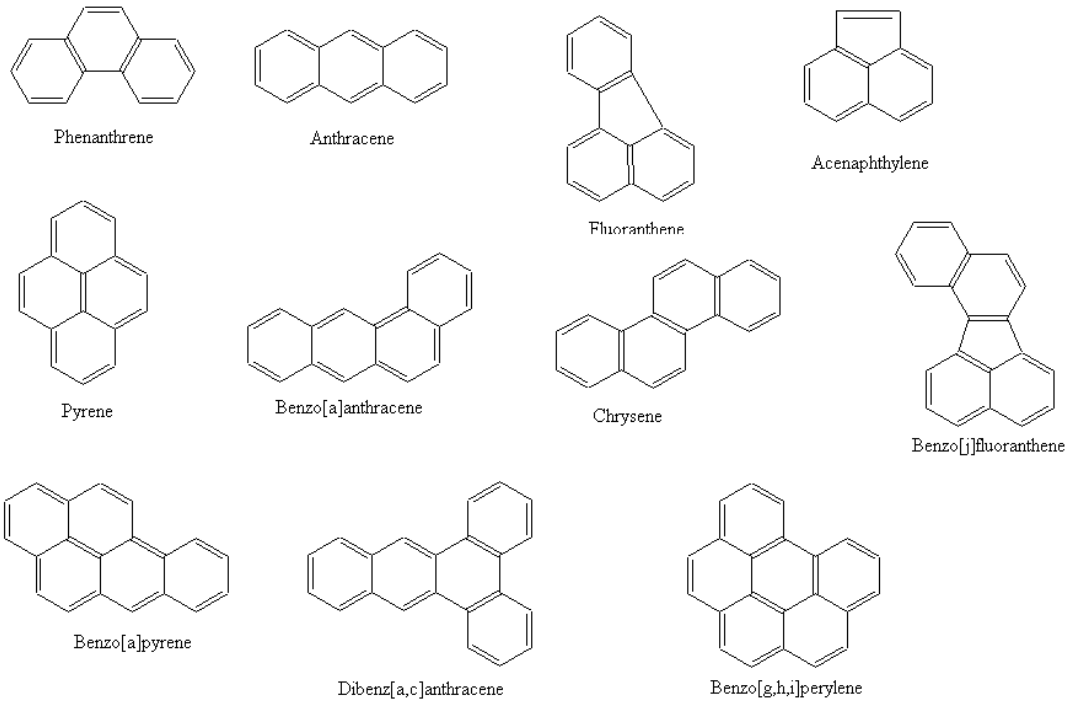


Figure 1-1: PAH molecules identified in pitch (Blanco et al., 1991).

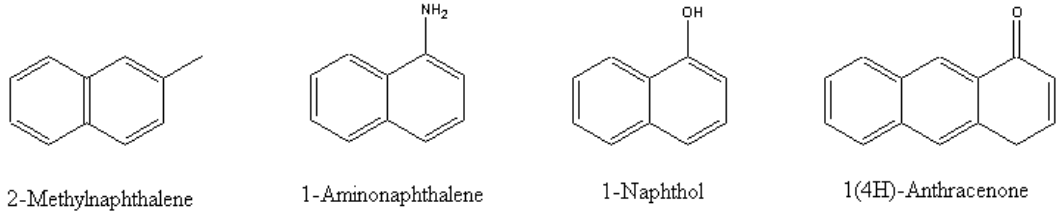


Figure 1-2: Examples of PAH substituted by alkyl or heteroatom side chains.

Figure 1-3: Example of heteroaromatic compounds. Shown in the simplest possible form.

Kershaw et al., 1993, determined average molecular structures of filtered (1 μm grit) petroleum pitch (Ashland, A240) and coal tar pitch (Koppers, Australia). The various atoms in the average molecules were established on the basis of molecular weight (VPO), elemental analysis and ^{13}C and ^{1}H NMR. Figures 1-4 and 1-5 show the average structures based on the results of Kershaw et al., 1993. Since the pitches were represented by only two molecules, not all the detected heteroatomic entities could be represented. Average structures are not capable of giving a full picture of the pitch but the figures do provide an overall insight into the nature and the main differences between the pitch types. The coal tar pitch consists of compact aromatic structures with few side chains. The structure is pericondensed, i.e. it contains carbon atoms situated within the aromatic ring system, as in pyrene. The petroleum pitch has a more open structure which, even though it is not totally catacondensed, shows a more linear orientation than coal tar pitch. It contains a relatively larger amount of alkyl side chains and these side chains are relatively longer than in coal tar pitch.

1.1.1. Empirical Quality Measures of Pitch

The complexity of the pitch has led to the development of empirical analysis methods for quality assessment. The most important purpose of these methods is to ensure that consistent pitch quality has been obtained. Based on decades of experience they can also be used to predict indirectly how a binder pitch will perform, while the empirical nature is kept in mind. The analytical procedures are described in Appendix A and a short description will be given here. Other empirical methods can be applied topitch and tar but they will not be treated in detail in this report.

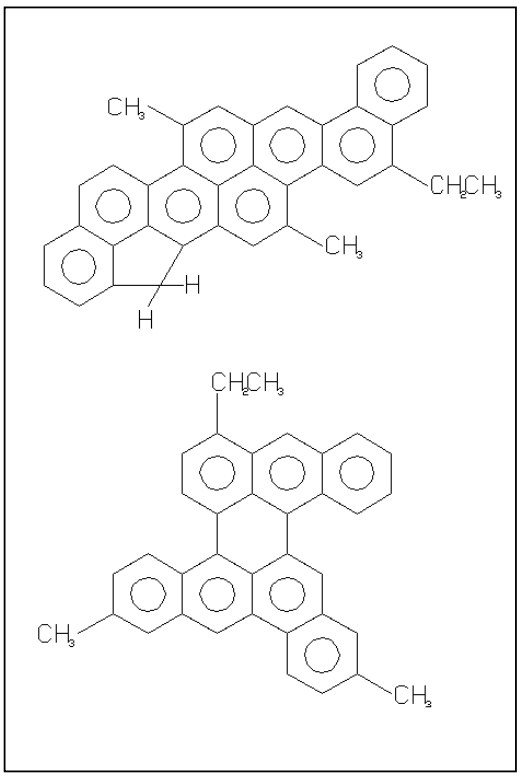


Figure 1-4: Proposed petroleum pitch structures. (Redrawn after data from Kershaw et al. 1993).

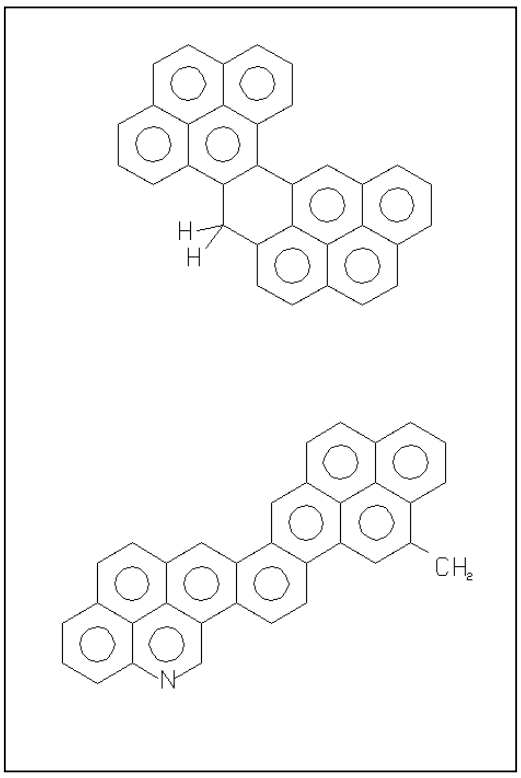


Figure 1-5: Proposed coal tar pitch structures. (Redrawn after data from Kershaw et al. 1993).

The softening point (SP) is historically one of the oldest properties tested on pitch. It is measured because this value gives indirect information about the viscosity and the distillation cut of the product. In actual use the pitch will be carbonized (Section 1.3). The coking value (CV) indicates the carbon residue of the pitch as well as the amount of gas liberated during the process.

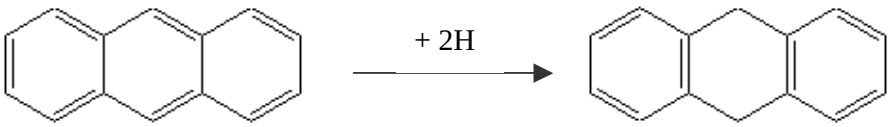
Solvent insoluble fractions are used to gain information about the pitch composition. The quinoline insoluble fraction (QI) has been mentioned above. Additionally, toluene insoluble (TI) is often measured. The exact function of this fraction cannot be entirely explained, but it is connected with the thermal history of the material. In some cases the solvent fractions are named according to another system. QI can be referred to as α-resin, the toluene insoluble/quinoline soluble fraction as β-resin and the toluene soluble fraction as γ-resin.

1.1.2. Hydrogen Donors and Acceptors

In Chapter 2 it will be described how pitches are manufactured experimentally including a thermal treatment step. Thermal treatment processes can introduce cracking and polymerization of the pitch components. One way to deal with these introduced reactions is to look at hydrogen donors and acceptors.

Hydrogen donors are capable of delivering hydrogen atoms which can stabilize free radicals formed by cracking. Thus, aromatic radicals formed by thermal cracking are prevented from recombining into larger aromatic species which will eventually form mesophase or coke. The stabilization of the aromatic components means that the pitch maintains its fluidity during mesophase formation and eventually form large anisotropic domains. The hydrogen acceptor ability of the pitch can be taken to be a measure of the ability of transformation of the pitch while the hydrogen donor ability represent the ability to stabilize the formed aromatic components and thereby maintain the fluidity of the pitch.

Pitch contains both hydrogen donors and acceptors. Díez et al., 1999, investigated the hydrogen donor and acceptor abilities of pitch by blending pitch with anthracene (hydrogen acceptor) or dihydroanthracene (hydrogen donor) and heating the mixture to 400°C. Equation 1-1 shows how anthracene is converted into 9,10-dihydroanthracene by addition of two hydrogen molecules. Both petroleum and coal tar pitches were investigated. It was found that the hydrogen donor ability of the petroleum pitches was higher than the value found for the coal tar pitches. The two materials had comparable hydrogen acceptor ability. For most of the pitches investigated by Díez et al., 1999, the hydrogen acceptor ability was higher than the hydrogen donor ability.



Anthracene 9, 10-dihydroanthracene Equation 1-1

1.2. Origin of Pitch

The origin and the thermal history of the pitches influence the sensitivity of the materials to thermal treatment. In the following section the processes acting as the main sources of pitch and tars will be described.

1.2.1. Coal Tar

Coal tar originates from coal. There are several ways to obtain a liquid product from coal but it is often obtained as a by-product of the production of other coal-derived products. Coal is a complex organic material derived from prehistoric plants and it can be classified in a number of subgroups. Depending on volatile content, calorific value, carbon and hydrogen content, the coal can be defined as anthracite, bituminous and lignite type of coal. The classification system differs from country to country and other names and further subdivisions exist. Coal contains moisture and volatile components and the amount varies from almost nothing in anthracite to more than half for the lower coal ranks. The components obtained by non-destructive solvent extraction are mainly n-alkanes with lower amounts of aromatic components, n-paraffins, cyclic alkanes and steranes (Speight et al., 1994). These components have great significance on the studies of the origin and the formation on coal, but the composition found in coal has little resemblance with the commercially obtained coal liquids. Although the word tar describes a black, heavy bituminous material, it is best to avoid using it about natural materials and to restrict the meaning to the volatile or near-volatile products of the destructive distillation of such organic substances as coal.

1.2.1.1 Gasification

Gasification of coal has been used to produce gas for either synthesis gas or fuel. The company which was the predecessor of Koppers Denmark, Tjærekompaniet, was founded in 1919 to deal with the tar by-product obtained from the production of town gas (Svendrup, 1994, and Aamand, 1984). The main product of this early processing was road

tar for pavement. Petroleum-derived products later substituted this application of coal tar pitch.

Coal can be gasified by use of steam, oxygen, air or hydrogen as gasification media, depending on the rank of coal and the desired gas product. Gasification can also be achieved by pyrolysis. In this case the process is very similar to the one described for coke ovens. Mostly, liquid by-products and especially tars are characterized as undesired in gasification processes. Schilling et al., 1981, reviewed twelve methods of gasification. Of the major processes listed in this work, only the Lurgi process and an experimental process applying heat from a nuclear reactor yield a significant amount of tar. In the Lurgi process the gasification takes place with oxygen and steam as gasification agents. The gasification temperature is between 760°-870°C. The tar is separated from coal dust, which is recycled to the reactor, and it is referred to as a medium temperature tar.

1.2.1.2 Liquefaction of Coal

Coal has been regarded as an alternative source of fuel in a future where the supply of oil might be more depleted. Research is carried out in the area of liquefaction as part of a strategic effort to be self-sufficient in emergency situations, by countries which have no oil production, but have access to coal. The main examples of commercial use of the processes are the Sasol Company in South Africa and Germany during the World War II. In both cases the liquid products are obtained by means of the Fischer-Tropsch synthesis in which carbon monoxide/hydrogen mixtures from gasification of coal are converted into liquid hydrocarbons. Aliphatic hydrocarbons are synthesized following the reaction shown in Equation 1-2.

$$(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O \qquad \text{Equation 1-2}$$

Liquid fuels can also be obtained directly from coal without gasification. This can be either by pyrolysis (see Section 1.2.1.3), solvent extraction or catalytic liquefaction. The oils resulting from these processes contain, as petroleum does, a heavy aromatic fraction. These substances have been studied under the name “coal asphaltenes” (Speight, 1994).

1.2.1.3 Coke Ovens

The most important process to the production of binder pitch is high-temperature coking of coal in order to produce metallurgic grade coke in by-product ovens. A short description will be given on the basis of literature sources (Gray et al., 1997, Speight, 1994, Franck et al., 1968, and Saint Romain et al., 1990)

The coke plant consists of coke batteries built up of 40-100 coking cells. The proportions of the coking cells vary between a length of 10-15 m, a height of 3-6 m and a width of 0.4-0.51 m, but a typical coke oven would be 12 m long, 4 m high and 0.5 m wide (Scaroni et al., 1985). 15-40 tons coal are loaded into the coke oven from the top. The coal is leveled by a leveling bar attached to a “pusher machine” whish is used for the later discharging of the finished coke. On each side of the coking chambers, fuel is fired to maintain the wall temperature in the range of 1040°-1100°C.

The coke oven can now be divided into two reactors: 1) A solid phase reactor where the coarse-grained coal blend is transformed into a fissured lump coke bed with the release of steam and primary tar vapors, 2) a gas phase reactor where the primary tar vapors and the steam are cracked by the effect of high temperatures generated by the walls and the coke cake top. In the solid phase the coke-forming reactions are taking place. The primary reactions consist of coal molecules depolymerisation and condensation to yield primary tar vapors, gas and coke. Gas and vapors are transported to the gas phase where secondary reactions are taking place. They consist of polycondensations, dehydrogenations and cracking off side chains leading to species stable at high temperatures (PAH). The volatiles develop further in the free space where extensive thermal degradation takes place, resulting in QI and pyrolytic carbon formation (Saint Romain et al., 1990). The coke ovens are carefully sealed so that the coal can be heated in the absence of air and to avoid emission to the atmosphere. Oxygen which enters the chamber due to air leakage does, however, favor oxycracking reactions which contribute to the final formation of QI.

The volatiles and the gas leave the oven chamber through an ascension pipe and enter a main collector. Here they are quenched with flushing liquor (thin recycled ammonia solution) and the temperature is dropped from about 980°C to about 90°C. This process condenses most of the tar out of the gas. The remaining tar components are removed by cooling the gas further down to around 20°C in the primary coolers. Ammonia, hydrogen sulfide, and lighter organic fractions are removed from the gas and the gas is used as fuel for the process. The flushing liquor (from the initial quenching) containing most of the tar is transported to a tar decanter, where the flushing liquor is separated from the tar and recycled to the main collector. Coarser coal or coke particles are removed from the tar by a slowly moving drag conveyor. The tar might be recombined with the tar that was condensed in the primary coolers. The product obtained by this process is the coal tar that is normally used in the production of binder pitch.

A full coking cycle lasts 14 to 24 hours. When the coal is fully carbonized the doors in both ends of the coke oven are removed and a ram pushes the finished coke from the chamber into a quench car. The quench car transports the coke to a tower where sprays of water are used to cool partially the coke before it is taken to a wharf where the cooling is completed before the coke is crushed, screened and taken to where it is to be used (Gray et al., 1997).

1.2.2. Manufacture of Coal Tar Pitch

Coal tar pitch is manufactured from coal tar by various distillation techniques. The manufacturing techniques have developed from atmospheric batch distillations to continuous vacuum distillation. The atmospheric batch distillation generally resulted in the product receiving addition thermal treatment and will be described briefly in Section 1.4.1. The Koppers Denmark (formerly Tarconord A/S) plant in Nyborg is run as a continuous vacuum operation and the process of this particular plant will be given as an example of a modern process. The information given in this section has been acquired by interviews with Koppers Denmark personnel and internal company documents.

The plant is designed to process coal tar and to fractionate it into chemical oils and pitch. Coal tar as received contains water so the first process step is the dehydration column. Here water and light oils are removed from the tar (C1 in Figure 1-6). The distillation takes place at 160°C and an absolute pressure of 1.05 bars. The heavy fraction containing the majority of the tar is transferred to the second distillation column, which is operated at a bottom temperature of around 360°C. Heating is achieved by recycling part of the bottom stream through a heater operated at 375°C. The top fraction is taken to a naphthalene distillation plant for further processing, while the bottom fraction is sent to the main vacuum distillation column (C3). Here it is distilled at a reduced pressure of 10 kPa and a bottom temperature of 340°C. Heating is obtained by recycling part of the bottom stream through a heater operated at 385°C. The described processes result in the coal tar being separated into several oil fractions, which can be used as feedstocks in chemical processes, and coal tar pitch, which is the main product.

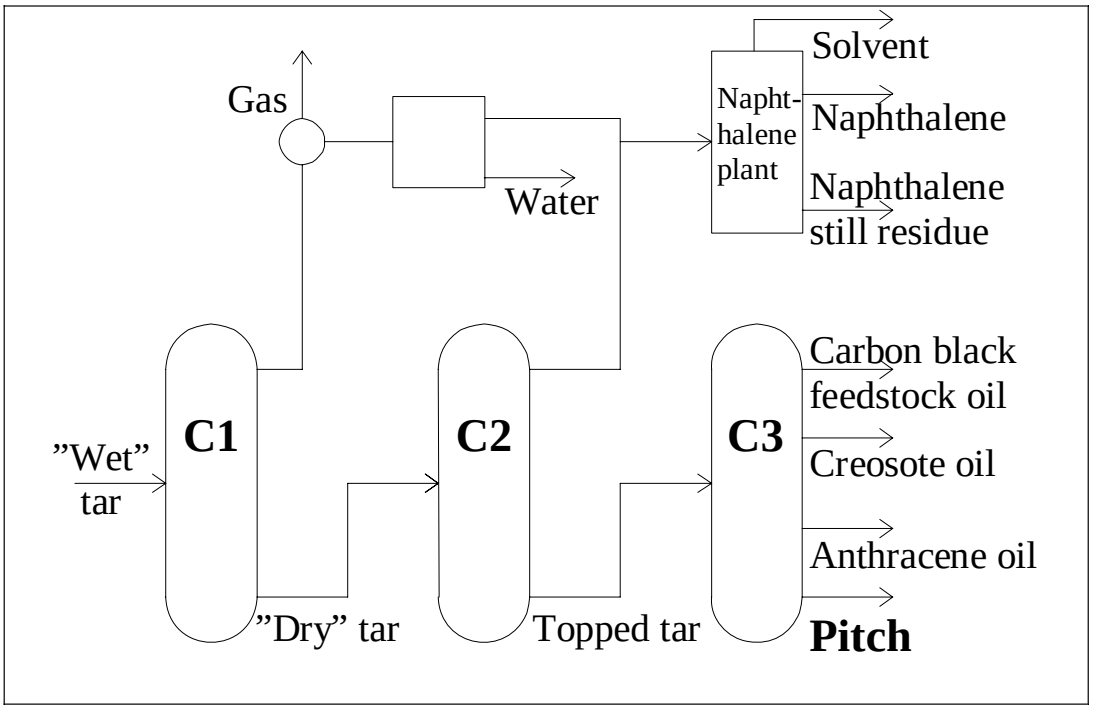


Figure 1-6: Schematic drawing of Koppers Europe's distillation plant in Nyborg.

1.2.3. Petroleum Pitch

Petroleum pitch and petroleum tars are by-products of several operations in a petroleum refinery. Depending on the structure of the refinery and the crude oil used as feedstock the properties of these products will vary. Petroleum tar and pitch are regarded as by-products of the oil refinery and the properties of these heavy products are therefore often skipped in descriptions of the process. In the following section, the main processes where tar- and pitch-like products are obtained will be briefly described.

1.2.3.1 Crude Oil Distillation

The terms tar or pitch are often used about the residuum obtained from the initial distillation of crude oil. The residuum may be liquid at room temperature (generally atmospheric residuum) or almost solid (generally vacuum residuum) depending upon the nature of the crude oil. When a residuum has been obtained from a crude oil and thermal decomposition has commenced, the product is usually referred to as pitch. The residuum often contains heptane (or hexane or pentane) insoluble fractions but, due to the limited thermal decomposition, it will generally be completely soluble in toluene. The fraction often contains ash-forming metallic constituents, including organometallic compounds as those of vanadium and nickel (Speight, 1991).

Even though the product which has been described here is usually implicit when petroleum pitch is referred to in the oil refinery it is a poor binder pitch. When compared to the coal tar pitch the thermal history of this product is less severe. This means that it has a much lower aromaticity than required of the product to perform satisfactorily during carbonization. The low aromaticity is indicated by low coking value and lack of toluene insoluble material. In addition this fraction contains the majority of sulfur and ash-forming components, which are unwanted in the binder pitch.

1.2.3.2 Thermal Cracking

Tar-like products can be obtained as by-products- of thermal cracking processes. These processes were the first means of altering the respective yields of crude oil fraction but are now described as obsolete. The processes range from mild cracking to actual coking. Petroleum hydrocarbons undergo cracking when subjected to temperatures above 350°C and actual coke formation is seen at temperatures down to 400°C and may be reduced by increasing the pressure (~25 bars) (Speight, 1991).

1.2.3.3 Catalytic Cracking

Catalytic cracking has replaced thermal cracking as the process for converting heavier fractions into fractions which can be used for gasoline. The main advantages of the process (from a refinery point of view) are that the product is more applicable in later processes, the product has higher "octane ratings" and that the catalysis requires lower temperature and results in higher cracking rates (Irion et al., 1991). The process yields a "slurry oil" or tar which might be interesting as a precursor for binder pitch purposes even though it is produced in lesser quantities than by the thermal process. Tar obtained from this process will have a low content of organometallic components. These components have to be removed from the feed to avoid catalyst deactivation.

1.2.3.4 Steam Cracking

The steam cracker tar is obtained as a by-product of steam cracking of naphtha or gas oil to produce ethylene (Rand et al., 1989). Ethylene cracker bottom is one of the better candidates for tar to yield acceptable binder pitch. The petroleum product used in the present study was obtained from this process (Chapter 2).

A hydrocarbon stream is heated, mixed with steam, and further heated to incipient cracking temperature (500°-650°C, depending on the feedstock). The stream then enters a fired tubular reactor where, with controlled residence time, temperature profile and partial pressure, it is heated from 500°-650°C to 750°-875°C. Saturated hydrocarbons in the

feedstock crack into smaller molecules in the radiant tube. Ethylene, other alkenes, and dialkenes are the major products (Grantom et al., 1987). Additionally, an aromatic cracker bottom fraction is obtained as a by-product.

1.2.4. Discussion of Pitch Sources

Tar and pitch are normally obtained as by-products of processes with other products as main goal. Thus, there is little control which processes have yielded products suitable as binder pitch. For some of the processes (here especially the petroleum-related products) it has been impossible to find descriptions of the heavy by-products in the literature available since the focus has been on the main, lighter products. There are, however, some important points to be made from the search in the literature.

Tar and pitch have little in common with the natural appearance of the original feedstocks in the case of products obtained from coal and petroleum. The product must have experienced a severe thermal process in order to reach the necessary aromaticity. Besides, it is beneficial if the metals content from the natural products is not transferred to the pitch.

The process during which the thermal influence is reached has to be highly controlled. Since binder pitch has the important quality that it is capable of becoming a fluid, at the temperatures where it is used, the process should not transform the product to coke. This means that the processes are operating in a very narrow window. An aromatic product which readily forms coke, but where the carbonization has not been initiated, should be obtained.

The process resulting in the best tar for binder pitch is the production metallurgic grade coke from coal. The process is unique by submitting the tar components to a very high temperature (>1000°C) for a short period while the product is in gas form. Droplets which are retained in the “reactor” or which have come near to the walls will already have formed carbon-black-like particles. This unique thermal treatment is probably more important to the success of this product than the origin from coal.

1.3. Uses of Pitch

1.3.1. Reduction Anodes for Aluminum Manufacture

The pitches described in this work are aimed at use as binders in reduction anodes for the aluminum industry. Anodes for this special application distinguish themselves from other carbon or graphite electrodes by the fact that they are consumed chemically during the process, and the short lifespan makes the economy an even more dominant factor in the preparation.

Aluminum is produced from alumina by an electrolytic reduction reaction. Alumina (Al_2O_3) is dissolved in a molten cryolite (Na_3AlF_6) where it is reduced by carbon from the anode. The principal reaction is given in Equation 1-3.

$$Al_2O_3 + 3/2\ C \rightarrow 2\ Al + 3/2\ CO_2 \qquad \text{Equation 1-3}$$

Alumina is obtained from naturally occurring bauxite, which is an oxide hydrate of aluminum ($Al_2O_3 \cdot xH_2O$) with impurities of silicates and iron oxide. The mineral is purified by the Bayer process. Bauxite is dissolved in a sodium hydroxide solution. Iron and silicate components maintain their solid form and are filtered from the solution. The pH is reduced with carbon dioxide and pure alumina is precipitated (Kofstad, 1987).

The electrolysis is carried out in a Hall-Héroult cell (see Figure 1-7). The reduction cell is mostly referred to as a pot and it is built up in a 9-14 m long, 3-4 m wide and 1-1.2 m high steel shell lined with thermal insulation. Within the insulating lining there is an inner carbon lining which acts as a cathode for the process. Current is supplied from current collector bars inserted in the cathode. Inside the carbon lining the molten fluoride electrolyte or bath is contained. In the bottom of the bath on top of the cathode the molten aluminum or “metal pad” is situated. Electrical current enters the cell through 18-32 prebaked carbon anodes or through a single continuous self-baking Søderberg anode. A crust of frozen electrolyte bath and alumina covers the molten bath and prevents oxidation

or “air-burn” of the anodes. A similar frozen crust ledge down the sides of the pot protects the steel frame from the highly corrosive bath (Haupin, 2000).

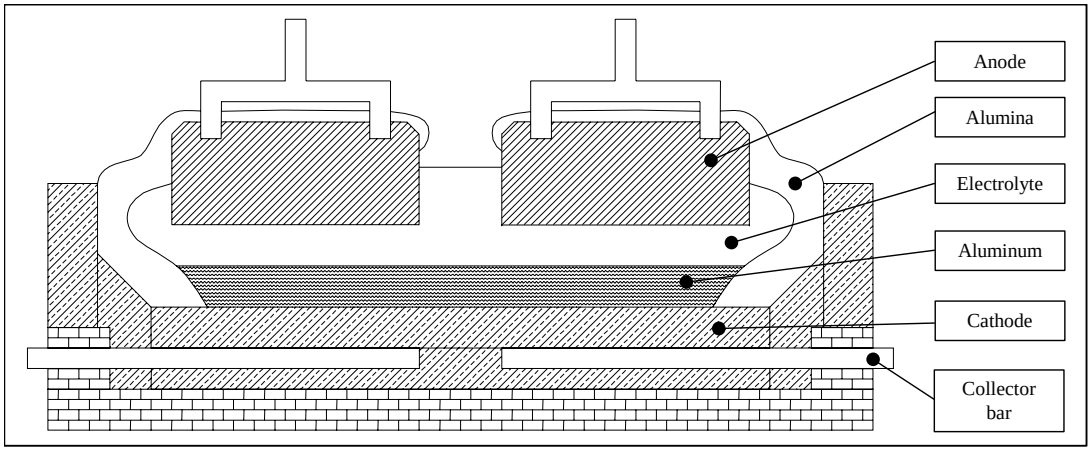


Figure 1-7: Schematic of Hall-Héroult cell with prebake anodes. Inspiration from Haupin, 2000.

The Hall-Héroult cell is built by use of two different technologies of anode preparation, the prebake and the Søderberg technology. For both types anode paste is blended from binder pitch, calcinated petroleum coke. The mixing is performed at a temperature above the softening point of the pitch, which allow it to wet the coke particles. Prebaked anodes also contain a fraction of recycled anodes called butts. When prebaked anodes are produced the anode paste is molded into shape and the anode blocks are baked at temperatures between 1000°-1200°C to allow carbonization of the pitch (see Chapter 6 for further description). In the Søderberg process the anode is contained within a cast and anode paste is added from the top. As the anode is being consumed, the paste is slowly lowered into the pot where the heat from the process carbonizes it before it reaches the cryolite bath.

The feedstocks for carbon anodes are calcinated coke, binder pitch and recycled anode material called butts. During start-up and at times where the anode production is subject to problems unbaked material called green scrap can also be recycled. The exact recipe of anode paste is optimized for every plant. Actual recipes are rarely published, but based on laboratory studies published in *Light Metals* the pitch levels are normally 13-20 percent with optimum conditions in the range of 15-16% (w/w).

The calcinated coke is usually obtained from petroleum refineries where it is manufactured by delayed coking. The coke should have a sponge or preferably a needle coke structure (Gary et al., 1994). Delayed coking is a semi-continuous process in which the heated feed is transferred to large soaking drums, which provide the long residence time needed to allow the cracking reactions to proceed to completion. The feed for these units is normally an atmospheric residuum, although cracked tars and slurry oils may also be used (Section 1.2.3). The heated feedstock enters one of a pair of coking drums where the cracking reactions continue. The cracked products leave as volatiles and coke deposits form on the inner surface of the drum. To make the operation continuous, two drums are used; while one is on stream, the other is being cleaned. The temperature in the coke drum ranges from 415°C to 450°C at pressures from 1 to 6 bars (Speight, 1991). Finally, the coke is calcinated at temperatures typically ranging from 1250°-1350°C (Mannweiler, 1995)

1.3.2. Electrodes

Coal tar pitch is used for other types of carbon based electrodes than anodes for the aluminum industry. The most important applications are the graphite electrodes for the electric arc steel furnace and the cathode lining of the aluminum pot. Since the carbon electrodes are consumed at a lower rate during these applications a demand for higher quality has developed. A crystalline structure which resembles more the perfect graphite structure is obtained.

The manufacture of electrical arc electrodes is described by Redmount et al., 1997. Green mix is prepared in a fashion similar to the green anode paste. The requirements of the coke are generally higher and the coke grade will be premium needle coke (i.e. the structure of the coke resembles needles due to large domains and a relatively high degree of crystalline order). Electrodes are formed as long cylindrical bodies by extruding the mix through conical dies. This ensures that the coke particle is crystallite-aligned. After the electrodes have been baked they are often impregnated with a low softening point pitch and rebaked. This is done to ensure a higher density of the electrodes. Finally, the electrodes are heated to about 3000°C to convert the material into graphite. Graphitization is accomplished by

passing electrical current through the rods under carefully controlled conditions. After graphitization the electrodes are machined to a desired, final configuration.

Cathodes in the aluminum industry are built up of carbon blocks. The quality of the carbon blocks ranges from the anode blocks, which were carbonized at ~1200°C to the electric-arc cathodes, which were graphitized at ~3000°C. The preferred material today is reported to be semi-graphitic carbon, where the aggregate is graphitized while the binder has only been heated to normal baking temperature (~1200°C). A thorough description is given by Sørlie et al., 1994.

1.3.3. Other Applications of Pitch

Different types of pitch are used as feedstock for a vast array of specialty carbons. The most well known applications are carbon fibers and C-C (carbon-carbon) composites.

1.4. Modification of Pitch Properties

1.4.1. Thermal Treatment

The phase “thermal treatment” covers a wide array of processes including transfer of thermal energy to the product. Historically, the term is used about a treatment which is far more severe than the one to be applied in the present work. In this section a short overview of the historical significance of the process is given, while a review of the literature directly relevant to the work will be given together with a description of the results in Chapter 2.

Romovacek, 1985, gives a review of the historical development in pitch manufacture. Originally, pitch was produced by atmospheric distillation in batch stills. The material was often strongly overheated due to poor heat transfer which led to formation of additional quinoline insoluble material. In the last half of the 20th century the distillation technique evolved into a continuous vacuum distillation, inspired by the petroleum industry. Because

of the lower temperatures and the shorter residence time the pitches received limited heat treatment and therefore did not contain any secondary QI. In order to reach the previous levels of QI, the vacuum distilled pitches could be given a controlled heat treatment at 380°-420°C.

Brooks et al., 1965, discovered mesophase and it was thus possible to distinguish between the primary QI formed in the coke oven and the secondary QI formed as a consequence of heat treatment. The formation of secondary QI was found to be bound together with the appearance of a liquid crystalline phase. It was moreover found that the primary QI gave the largest benefits and heat treatment was abandoned.

In recent years, new types of thermal treatments have developed. The thermal treatment is applied earlier in the production scheme and the temperatures are kept below the level where mesophase is formed. Examples of these experimental approaches will be described in Chapter 2. The experimental efforts have been reported to have led to a commercial product (Bermejo et al., 1997), but the method is still being investigated.

1.4.2. Oxidation

Oxidation or air blowing has been used as a means to modifying pitch properties. The process is assumed to lead to cross-linking and condensation reactions and to suppress the growth of mesophase spheres in the isotropic matrix. Compared with thermal treatment, oxidation is believed to lead to cross-linking as well as the formation of large planar molecules while thermal treatment only leads to planar molecules (Fernández et al., 1994). The method has been investigated as a method for obtaining high softening point, isotropic pitches as precursors of carbon fibers (Maeda et al., 1993).

1.5. Typical Abbreviations Used in the Thesis

The area of pitch science has its own terms and abbreviations. In the following, the meaning of the commonest will be listed along with abbreviations which are introduced in this work.

α-resin	Quinoline insoluble fraction of pitch
β-resin	Quinoline soluble, toluene insoluble fraction of pitch
γ-resin	Toluene soluble fraction of pitch
Air perm.	Air permeability
Air rx.	Air reactivity
BAD	Baked apparent density
Cal.	Calculated
CO_2 rx.	CO_2 reactivity
CP/MAS	Cross-polarization
Crush. st.	Compressive strength
CT	Coal tar
CTE	Coefficient of thermal expansion
CTP	Coal tar pitch
CV	Coking value
DA	Diode array
ER	Electrical resistivity
Exp.	Experimental
Flex. st.	Flexural strength
Frac. st.	Fracture energy
GAD	Green apparent density
GC	Gas chromatography
GC-MS	Gas chromatography with a mass spectrometry detector
He dens.	True density
HPLC	High performance liquid chromatography
HT	Heat treatment (or thermal treatment)
In situ CV	Coking value of pitch in anode

IP	Irregular patch (Section 4.4)
IR	Infrared spectrometry
MIX	Combined coal/petroleum pitch (Chapter 6)
NMP	N-methyl-2-pyrrolidinone
NMR	Nuclear magnetic resonance
PAH	Polyaromatic hydrocarbons
PP	Petroleum pitch
Primary QI	QI originating from the coke oven process
QI	Quinoline insoluble fraction of pitch
RI	Refractive index
SD	Straight distilled (used about pitch obtained directly from tar by vacuum distillation)
SEC	Size exclusion chromatography
Secondary QI	QI originating from thermal treatment undergone by the material after it has left the coke ovens
Shrink.	Shrinkage
SP	Softening point
SP/MAS	Single-pulse
Static ela.	Static elasticity
Th. cond.	Thermal conductivity
THF	Tetrahydrofuran
TI	Toluene insoluble fraction of pitch
TS	Toluene soluble fraction of pitch
VPO	Vapor pressure osmometry

2. Thermal Treatment in the manufacture of Pitch

2.1. Literature Study

The idea of thermal treatment of tar or pitch is not new. Before the vacuum distillation of coal tar became the leading technology for tar processing, coal tar was distilled into pitch by use of atmospheric batch stills. In the stills all coal tar pitch received a variable and largely uncontrolled amount of thermal treatment, which often led to secondary QI in the finishing product (Section 1.4.1). Continuous vacuum distillation meant that the amount of thermal treatment in the manufacture was minimized. The change in technology was gradual and from the fifties to the early eighties both technologies coexisted. This opened up a discussion about the significance of thermal treatment, which mainly centered around the usefulness of secondary QI or mesophase in binder pitches (see Chapter 4 for further discussion of mesophase and QI and Sections 1.2.2 and 1.4.1 on distillation technique).

The present study differs from the majority of published literature in that the goal is *not* to produce a pitch with a substantial mesophase content. During this study a very limited amount of literature concerning thermal treatment of tar or pitch has been found, where the primary target of the treatment was *not* the formation of either mesophase and/or secondary QI. In the following section, literature on thermal treatment under conditions where the formation of mesophase and secondary QI is limited will be reviewed.

2.1.1. Coal Tar Pitch

McHenry et al., 1993, studied the behavior of tars during thermal treatment. Four tars were selected as feedstock, two tars with a natural QI of approximately 2.5% and two with a natural QI in the range of 7%. The tars were first distilled to a softening point of 40°C, then thermally treated at 390°C under atmospheric pressure for up to 12 hours and finally vacuum-distilled into a 110°C SP (softening point) pitch. Without thermal treatment all four tars yielded a pitch with around 15% β-resins. Thermal treatment increased the amount of β-resins to around 20% in the high QI pitches and 23% in the low QI pitches. Although the extended thermal treatment resulted in minor QI increases, any mesophase

which was formed was not visible by optical microscopy. The viscosity was increased with increasing treatment severity for all samples. This effect was most pronounced for the high QI pitches. A small increase in coking values was also observed.

In a recent study by Malmros et al., 2000, pitch was produced from coal tar including a tar thermal treatment following the same procedure as used in the present work (see Section 2.2 for a detailed description). The original tar was "topped" (typically by 20%) by distillation under vacuum. The thermal treatment was conducted at temperatures between 372° and 404°C for up to 8 hours. The material was further distilled to yield a 120°C softening point pitch. The investigation aimed at finding a procedure for increasing the pitch yield from a given tar (and if possible the TI and the CV as well) without producing mesophase in the product and without harmful effects on the properties of bench scale, laboratory, prebaked aluminum smelting anodes made from the products.

Malmros et al., 2000, found that the pitch yield increased both with increasing treatment temperature and duration. At constant temperature the yield was found to increase linearly with the soak time within the first eight hours. Pitch properties such as secondary QI, TI, and CV were found to be functions of the increase in pitch yield. TI and CV were linear functions while the secondary QI showed a steep increase at a yield increase of about 6%. The properties belonged to the same population regardless of whether the yield increase was obtained by high soak temperature or long soak duration. At 404°C all measured properties were increased at a high rate making the process much more difficult to control. The authors recommended a treatment at 387°C for six hours as the optimum treatment with the smallest risk. Bench scale anodes made from pitch, which had received this treatment, showed properties comparable to anodes obtained from control pitches.

The effects of primary QI in the precursor tars on the yield increase, the amount of secondary QI and the amount of mesophase were also investigated. It was found that the yield increase was slightly reduced with increasing primary QI content. This effect was not due to the primary QI particles themselves, but rather to the fact that this parameter is linked in a direct relation with aromaticity. A more aromatic precursor has less potential for thermally induced ring closure and side chain removal and could be expected to have a

reduced sensitivity to thermal soaking. The experiments where the treatment was carried out at the highest temperature (404°C) showed mesophase formation in all the resulting pitches. An interesting finding was that the amount of secondary QI in the resulting pitch increased with the amount of primary QI in the precursor tar. The amount of visible mesophase, on the other hand, showed a decreasing tendency (Malmros et al., 2000).

Unlike the description in most of the literature, no thermal treatments were conducted on the finishing pitches, but on tars in which a part of the oil had been removed before the thermal treatment. An important question in this process was how much oil should be removed prior to the thermal treatment. According to Malmros et al., 2000, the answer is as little as possible. Pitch with a target softening point of 120°C was produced from tars where 7 to 52 % oil was removed before a thermal treatment for six hours at 390°C. The results were based on three different tars and show that the less oil removed before the heat treatment, the higher the resulting pitch yield. Additionally, if more than 30% oil was removed, mesophase started to appear sooner in the resulting pitches. The amount of mesophase accelerated with the amount of oil removed. This result strongly indicates that the lower boiling, lower molecular weight components play an important role during thermal treatment and that they help to suppress mesophase development in the resulting pitch.

Bermejo et al., 1995, subjected two pitches produced from the same tar to extensive testing and analysis. One of the pitches was prepared by straight vacuum distillation and the other pitch was prepared by thermal treatment of the tar at 385°C for 11 hours before distillation to make pitch. The study aimed at examining the influence of the volatile fraction on pyrolysis but contained detailed studies of tar thermal treatment versus straight distillation. The first conclusion drawn on the basis of the data was that the content of β-resins and the C/H ratio were both increased by the tar thermal treatment. The pitch yield of 108°C SP pitch (the softening point was found experimentally by the authors using the Krämer-Sarnow method but it is here calculated into the result, which would have been found if the Mettler method had been applied, using DIN 52025) was increased from 46.3% to 55.3%. This data indicates that the tar thermal treatment results in more condensed aromatic molecules. The thermally treated pitch contains more light components than the vacuum-

distilled pitch. This was found both by GC and SEC analysis. The pitch yield was increased, because some of the lower molecular weight components had combined in higher boiling components by polymerization, and because the higher amount of polymerized components had to be balanced by a higher content of volatiles, in order to maintain the same softening point.

Bermejo et al., 1995, examined the hydrogen donor and acceptor abilities of the two pitches by letting a sample react with anthracene and 9,10-dihydroanthracene, respectively (see Section 1.1.2). Both the donor and the acceptor abilities were reduced to half of their initial value by the thermal treatment, but the ratio between the two parameters was constant. The amount of aromatic hydrogen (measured by FT-IR) was increased and the amount of aliphatic carbon decreased. These measurements were interpreted as interaction between the donor and acceptor components in the sample. By extrography it was found that the thermal treatment resulted in a decrease in compounds bearing basic nitrogen and phenolic groups. At the same time the content of aromatic components was increased. The extrography method was described in detail by Granda et al., 1990. This study supports the findings of Bermejo et al., 1995, but the conclusions are based on samples which have been thermally treated under conditions not clearly described in the publication.

An interesting result presented by Bermejo et al., 1995, which was obtained by hot-stage microscopy, was that pitch produced from thermally treated tar formed mesophase when heated to 370°C, while the vacuum-distilled pitch had to be heated to 410°C before small spheres were formed. Thus, the thermal treatment resulted in the formation of mesogenic molecules, which readily form mesophase once heated to the necessary temperature. During coke formation it was seen that the pitch from thermally treated tar formed larger-size optical textures than the straight distilled pitch.

The results reported in the work of Bermejo et al., 1995, show that thermally treated tar yields a pitch differing from a straight distilled pitch produced from the same tar. The differences must be explained both by the formation of larger mesogenic species and a higher content of volatiles in the pitch.

The conclusions were supported in a similar work from 1997 (Bermejo et al., 1997). In this work three materials were compared: a straight distilled pitch, a pitch manufactured from the same tar including an 11-hour treatment at 380°C of the tar and a petroleum pitch (A240 from Marathon Ashland). In this article it was stated that all three pitches were obtained from commercial sources. As in the previous work the main modification introduced by the thermal treatment was a higher amount of condensed aromatics, a lower content of heteroatoms (N, O) and a higher content of volatiles, which had to be included to give similar softening points.

The studies described here show that thermal treatment of tar as received or of topped tar can improve the pitch yield, the coking value and the toluene insoluble of the resulting pitch. This can be achieved without creation of secondary QI and without formation of mesophase. The three studies (McHenry et al., 1993, Malmros et al., 2000 and Bermejo et al., 1995) used treatment temperatures of 380°C and 390°C to obtain their results. It was apparent that this range of temperature has a significant influence on whether or not mesophase will be found in the final pitch.

These findings raise the question whether there is a minimum temperature for changes in the pitch. Turner, 1987, conducted a study of the influence of storage temperature on molten pitch. Increases in softening point, C/H ratio, CV and TI were seen as a result of keeping the pitch at 220°C. Thermally treated and vacuum-distilled pitches were examined and it was seen that the thermally treated pitches were more sensitive to additional thermal treatment, thus keeping the temperature low. This finding for pitch heat treatment during production, held at such a low temperature as 220°C, was supported by Koštál et al., 1994. As part of a kinetic study of β-resin and secondary QI formation in the temperature range of 230°–410 °C, a pitch was thermally treated at 230°C. It should be noted that the treatment time in both studies was several days, but a clear effect was achieved.

2.1.2. Petroleum Pitch

Studies of thermal treatment of petroleum pitch and tar have almost exclusively aimed at producing pitch with a very high content of mesophase. For this reason there is a large

amount of literature reporting heat treatment at temperatures of 430°C and above. A few of these studies do, however, cover experiments at temperatures down to a range of 380°-400°C.

Dickakian conducted series of thermal treatments on catalytic cracker bottom distillate fractions and residues as well as steam-cracker tars (Dickakian 1986a, 1986b, 1986c).

The catalytic cracker bottom distillate fraction with a boiling point ranging from 420°C to 520°C was subjected to extensive study (Dickakian 1986a). This fraction contained no ash or asphaltenes and it had a coking value of 1% (at 550°C). Separate treatments at 400°, 410°, 420°, 430° and 440°C were carried out at atmospheric (N_2) pressure for one hour. The development of the n-heptane, toluene, pyridine and quinoline insolubles (HI, TI, PI and QI) with treatment temperatures is depicted in Figure 2-1. The treatment temperature had to be raised above 420°C before any secondary QI material was formed. The influence of the soak time was investigated at treatment temperatures of 420°C and 430°C. All insoluble fractions were increased with increasing soak time (Figure 2-2). It was further seen that the amount of aromatic carbon and hydrogen increased (^{1}H and ^{13}C NMR) with increasing treatment temperature, while benzylic and aliphatic protons decreased, indicating dealkylation of the alkylaliphatic side chains combined with polymerization and condensation of the aromatic rings. It was also found that a relatively high temperature (around 430°C) was required to produce a pitch with a high mesophase content.

The catalytic cracker bottom was split into finer boiling range fractions by distillation (Dickakian, 1986b). It was noted that the aromatic ring number, the pitch yield and the TI had increased with increasing initial boiling point range. The residue (boiling range >510°C) differed from the distillate fractions by having an ash content of 0.11%(w/w), measurable HI and CV and higher molecular weight and C/H ratio. Pitch samples were manufactured by a three-hour treatment at 430°C and vacuum stripping of the distillate fractions. As a result of the treatment, the distillate fractions gave a higher pitch yield, higher TI and no QI in the pitch.

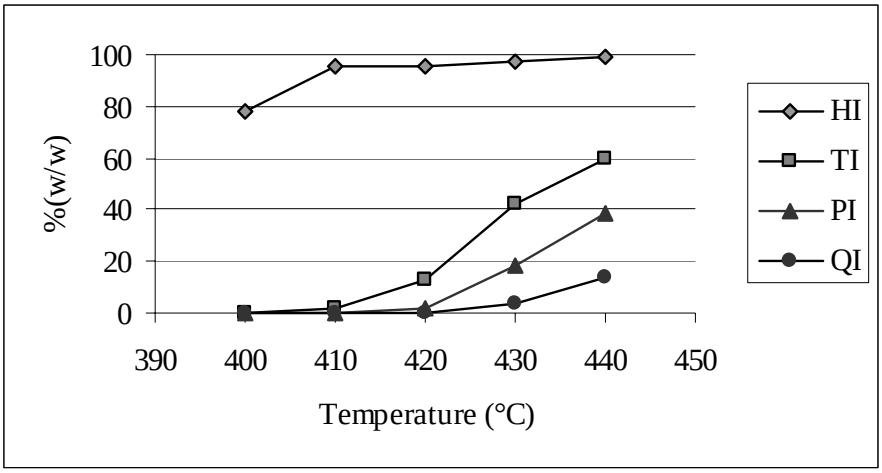


Figure 2-1: The development of the n-heptane, toluene, pyridine and quinoline insolubles (HI, TI, PI and QI) of catalytic cracker pitch from distillate fraction after a one-hour treatment (data from Dickakian, 1986a).

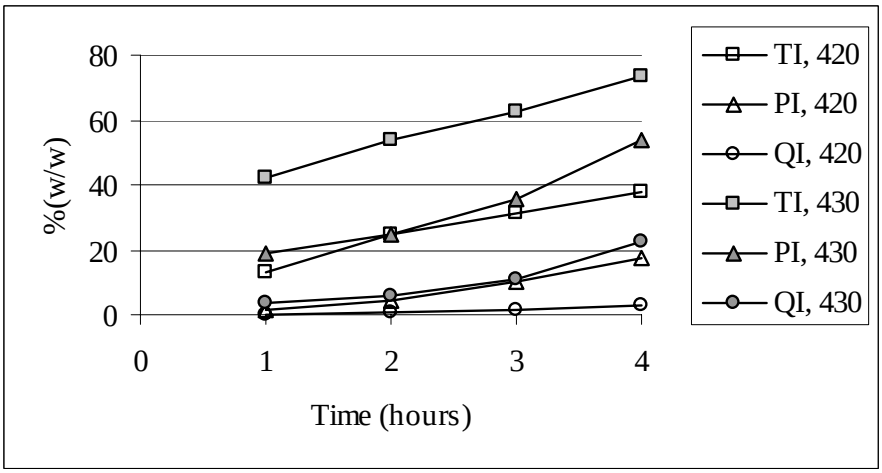


Figure 2-2: The development of the toluene, pyridine and quinoline insolubles (TI, PI and QI) of catalytic cracker pitch from distillate fraction as functions of soak time at 420°C and 430°C (data from Dickakian, 1986a).

Steam-cracker tar is a by-product of steam cracking of naphtha or gas oils to produce ethylene (Section 1.2.3.4). It can be turned into a pitch by vacuum or stream stripping, thermal or catalytic oxidative polymerization at 229°-260°C, or by a thermal process at 370°-450°C at atmospheric nitrogen or hydrogen pressure (Dickakian, 1986c). The author recommended a thermal treatment in the temperature range of 380°-430°C. When thermally treated at 380°C, the amount of aromatic carbon (by NMR) was increased. The

rate of increase was high for the first three hours with the amount of aromatic carbon going from a starting point of 70 to 74 % after three hours (atom %). After this initial rapid rate of increase, the rate decreased resulting in approximately 76.5% carbon in aromatic environment after 15 hours of treatment. From other experiments it was found that the aromaticity increased with increasing temperature. In summary Dickakian, 1986c, found that high softening point, high coking value and aromatic pitches can be prepared from steam cracker tar.

Azami et al., 1994, treated a petroleum pitch thermally at 390°, 410° and 430°C for varying soak times as part of a study of mesophase formation kinetics. The data indicated that mesophase formation followed simple, autocatalysis-type reaction kinetics after a critical level of 5% mesophase had been reached. The following conclusion based on the data is beyond the original intentions of the authors. A review of the experimental data given in this work shows that there is a certain initiation period before the mesophase formation starts. When treated at 390°C, the pitch showed no mesophase during the first three hours. It was possible to keep the sample at 410°C for 15 minutes and at 430°C for five minutes without any mesophase formation. The delay can be explained by considering the formation of the nematic liquid crystal as a physical process rather than a chemical process. Once the pyrolysis chemistry has established the requisite concentration of suitably shaped and sized molecules, then the nematic liquid crystals are formed consequently (Marsh, 1974).

The article by King et al., 1968, concerning binder pitch, petroleum material and thermal treatment is classic in the field of thermal treatment of petroleum pitch. Coal tar pitch for Søderberg anodes was compared to a petroleum pitch which was derived from a petroleum tar (described as a petroleum thermal tar) by vacuum distillation to 50% bottom yield (385°C cut-off point). It was found that the petroleum pitch contained no QI or TI and which it had a poor coking value. The general negative evaluation was confirmed by preparation and evaluation of test anodes. Attempts were made to improve the petroleum pitch by subjecting the precursor tar to a 3.5-hour treatment at 470°C under 12 bars of N_2 pressure. It was reported that approximately 5 % of the material was lost due to coke formation on the walls of the reactor. This treatment yielded both TI and QI in the resulting

pitch that was obtained by vacuum distillation. Even though the treatment yielded a pitch resembling the properties of coal tar pitch, it did not perform as well as a binder. Moreover, it was found that a pitch derived from catalytic cracker bottom performed better as binder although the analytical test results for this product were inferior. It was concluded that the coal tar pitch was superior to the petroleum products, mainly due to a higher number of aromatic rings per molecule.

2.1.3. Dual Origin Pitches and Thermal Treatment

Few articles were found on pitches derived from both petroleum and coal tar in one product. In the US combined coal tar/petro-pitches are, however, already commercial products. McHenry, 1997, and Wombles et al., 2000, described the development of a pitch product containing up to 15 % petroleum-derived material. The pitch was reported to give no significant difference in anode quality or performance. A second pitch product containing up to 40% petroleum material was reported to give slightly inferior anode density and carbon consumption compared to pure coal tar pitch. However, anodes produced from this pitch did not pose any significant problems and the PAH emissions were considerably reduced. Both products have proven that the coal tar/petro-products can be competitive with pure coal tar products and that a reduced content of PAH is a potential advantage.

Marathon Ashland Petroleum Company material was part of the final product, which was described by McHenry, 1997, and Wombles et al., 2000. This company is well known for producing petroleum pitches with relatively high aromaticity and coking value, and the authors mention that special care should be taken to choose a suitable petroleum source. In the earlier paper describing the development of the pitch types (McHenry, 1997), it was mentioned that up to 75 petroleum materials were characterized by I_A, NMR, CV and sulfur level before a suitable pitch precursor was found.

Pérez et al., 2000, investigated blends of a coal tar pitch and two different petroleum pitches. The authors concluded that coal tar and petroleum tar components can interact when heated together. These conclusions were based on thermal analysis (TG/DTG and

DSC) and optical microscopy. Thermal analysis showed that the peaks of maximum weight loss for this material cannot be calculated by combining the curves for the pure materials so an interaction is therefore indicated. This was further confirmed by optical microscopy, which revealed that high capacity of the petroleum material to form mesophase was reduced by addition of coal tar pitch.

The literature study reveals that coal tar/petro-pitches might perform comparably to a pure coal tar product and display the described synergic effects.

2.1.4. Kinetic Studies

The increase in solvent fractions of pitch during heat treatments has been analyzed by various reaction kinetic models. In order to apply reaction kinetics to the thermal processes, it is necessary to assume that solvent fractions (α-, β-, and γ-resins) act as separate "components" which are sequentially reacted to form other solvent fractions. Koštál et al., 1994, found that the "reactions" ($\gamma \rightarrow \beta \rightarrow \alpha$) followed a simple first order reaction kinetic in the temperature range 230°C to 410°C for a coal tar pitch, while Py et al., 2000, found that the formation of TI rather followed a second order kinetic ($2\gamma \rightarrow \beta \rightarrow \alpha$). In the work of Py et al., 2000, both a coal tar pitch and a petroleum pitch were examined at 400º, 430º and 450°C. The studies indicate that the same results can be obtained by treatments different combinations of soak time and temperature.

2.1.5. Conclusion on the Literature Study

The literature contains few works on thermal treatment intended to stop short of optical mesophase formation. However, it has been shown that it is possible to alter the physico-chemical characteristics of a pitch or tar and thus make it more attractive for binder pitch application. TI and CV in particular can be increased by thermal treatment. There are also some indications of increased pitch yield.

At the molecular level thermal treatment tends to lead to a decrease in aliphatic side chains and a decrease in basic nitrogen, phenolic and benzylic groups. At the same time

cyclization and elimination increase the amount of aromatic hydrogen and carbon. This information is interpreted as dealkylation of smaller side chains combined with polymerization and condensation of aromatic rings.

Very little information was found on the subject of mild thermal treatment of petroleum-derived pitches or those of coal tar combined with petroleum-derived materials. Most work on petroleum-derived material has been aimed at producing pitches with a high concentration of mesophase, which means that it has been carried out under severer conditions than the ones likely to be successful in this study. Few articles cover the subject of coal/petroleum materials and none of these include mild thermal treatments.

2.2. Experimental Procedure

The following section describes the experimental methods, which were used to produce the pitches in this study. The purpose of the study was to investigate the influence of a mild thermal treatment in the manufacture of binder pitch. In this context a mild treatment is defined as a treatment which does not lead to appreciable mesophase formation.

Figure 2-3 shows a schematic representation of the experimental production procedure. The tars were first topped, so that the 10-20% lowest boiling part of the as-received tar was removed by simple distillation, this is known as “topped tar”. In the experiments with combined materials, the materials were blended after the topping process step. Afterwards the combined, topped tars were thermally treated under a nitrogen pressure of six bars. The final step was vacuum distillation to obtain a target 120°C softening point pitch.

2.2.1. Topping of Tar

Three tar products were used for the thermal treatment experiments. All the tars were received as commercial feedstocks from Koppers Denmark. The properties of the materials as received are listed in Table 2-1. The first (F98015) was a petroleum tar (an ethylene cracker bottom), which was topped in the laboratory before the treatment. Two other materials, a topped coal tar (F98017A) and a topped petroleum tar (F98020), were obtained

from Koppers Europe's distillation plant in Nyborg, where they were taken from the bottom stream of the second distillation column (Figure 1-6).

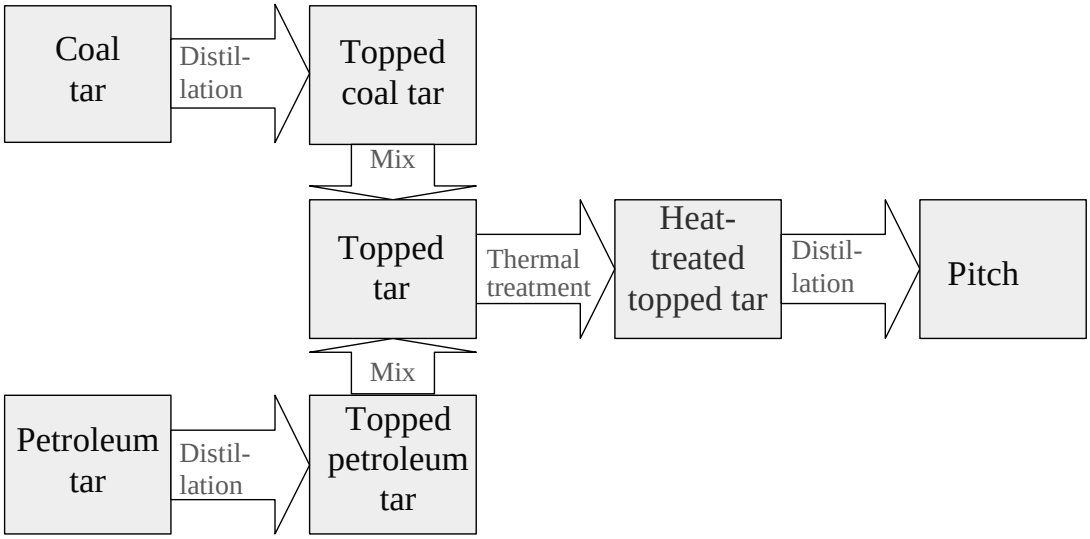


Figure 2-3: Schematic of the experimental production of pitch.

A comparison between the topped coal tar and the petroleum as received and topped can be made on the basis of the data in Table 2-1. Both TI and CV were lower for the petroleum materials than for the topped coal tar. The two petroleum materials contained practically no QI, and the amount of metal components in the tars was very low compared to the topped coal tar. Elementary analysis revealed that the petroleum tar contained less nitrogen and oxygen than the topped coal tar. The sulfur content was at the same level for all materials. The elementary analysis was carried out in DB Lab, Odense. All the results were given in relation to the original sample, so that the percentage did not necessarily add up to 100. The detection limit of the oxygen measurement was 0.15 %, representing one count in the element analyzer. The result of 0.34 was derived from two counts so that the differences between the petroleum materials were within the margin of error. The petroleum tars contain more hydrogen than the topped coal tar used in this study.

Properties	Unit	Petroleum tar F98015	Topped petroleum tar F98020	Topped coal tar F98017A
QI	%(w/w)	0.1	0.2	4.7
TI	%(w/w)	2.5	5.7	16.2
CV	%(w/w)	26.8	30.7	38.0
Element analysis				
C	%(w/w)	92.62	93.14	92.67
H	%(w/w)	6.44	6.31	4.80
N	%(w/w)	0.22	0.21	1.31
S	%(w/w)	0.46	0.49	0.46
O	%(w/w)	0.34	<0.15	0.82
C/H	(n/n)	1.20	1.23	1.61
Metal analysis (ICP)				
Sulfur	%(w/w)	0.52	0.59	0.52
Nickel	ppm	3	7	5
Vanadium	ppm	1	<1	2
Aluminum	ppm	9	4	57
Calcium	ppm	4	5	52
Iron	ppm	4	7	89
Magnesium	ppm	<1	1	9
Manganese	ppm	<1	<1	2
Sodium	ppm	<1	7	121
Lead	ppm	-	<1	138
Zinc	ppm	-	3	151

Table 2-1: Properties of precursor tars and topped tars used as feedstock for the study.

The sample used in the pure petroleum pitch series was received as a tar (F98015) and distilled in the laboratory prior to the thermal treatment. This distillation was carried out in order to avoid flash distillation during the thermal treatment. The resulting tar will be referred to as topped tar.

The distillation was performed under vacuum to reduce the heat exposure of the tar at this step. The tar was preheated to approximately 100 °C to allow 6-8 kg to be transferred to a ten-liter, three-neck distillation flask. The equipment for the distillation is shown in Figure 2-4. 10-20%(w/w) was removed by distillation and the maximum temperature at this step

was 160 °C. The topped tar was then divided into smaller portions in one-liter distillation flasks.

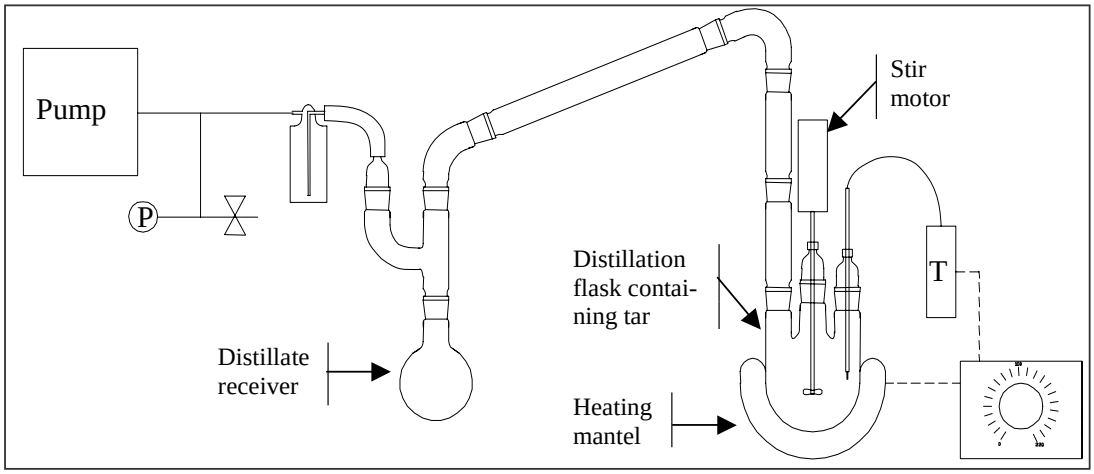


Figure 2-4: Experimental set-up for vacuum distillation.

The two topped tar samples (F98020 and F98017A) were received as already topped from Koppers Europe's distillation plant in Nyborg. The normal operation of the plant is described in Section 1.2.2. The topped tars provided for the study were taken from the bottom of the atmospheric distillation column (C2, Figure 1-6). The maximum temperature the tar had been exposed to at this point was 375°C in the heater. As described in Section 1.2.2 the plant is designed for processing coal tar, but occasionally it is used for distilling petroleum tar. For this operation temperatures are generally lower. The highest temperature experienced by the petroleum tar of the experiment was 335°C at the bottom of column C2 and 340°C in the heater of C2. Based on plant data it was calculated that 19.9 %(w/w) oil was distilled from the topped coal tar relative to dry tar and that 14.2 %(w/w) oil was distilled from the petroleum tar.

2.2.2. Heat Treatment

A one-liter distillation flask with the topped tar was preheated to 100 °C to reduce the viscosity. It was placed in a steel container as shown in Figure 2-5. The container was sealed and placed in a ceramic oven (Figure 2-6). The content of the vessel was mechanically agitated with a stirrer running in a gland tube through the lid (Figure 2-5).

The pressure was maintained at five bars above atmospheric pressure (N_2). Off-gases were allowed to escape from the vessel into the stirrer gland where they were removed by a purge stream of ca. 0.5 l/min nitrogen. The purge stream was connected to the reactor by a T-tube. The temperature in the tar was monitored by a thermocouple located through a separate tube.

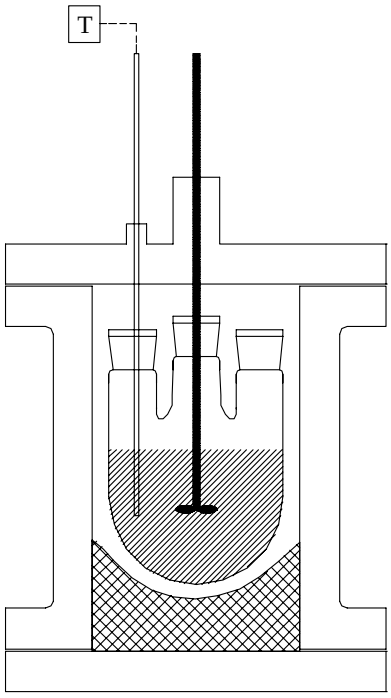


Figure 2-5: The distillation flask located in the pressurized container.

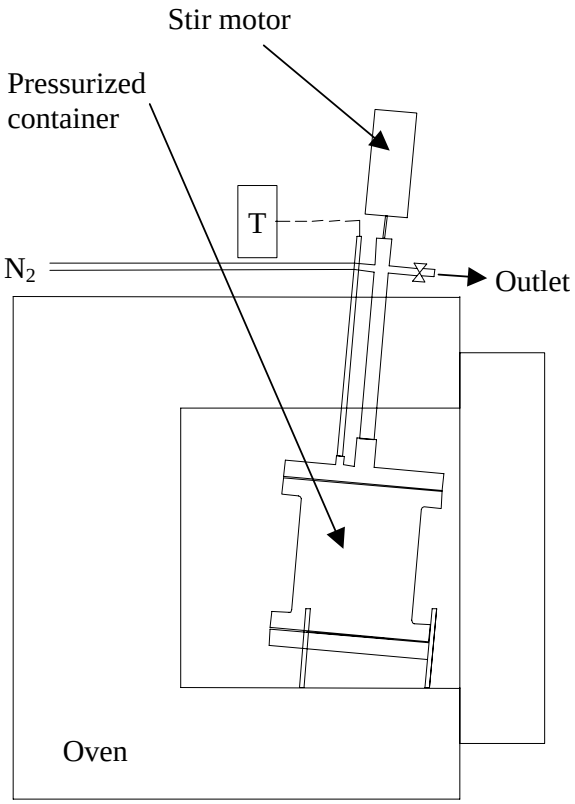


Figure 2-6: The pressurized container located in the oven.

At the start of each experiment the container was pressurized with nitrogen gas. The temperature in the chamber was gradually increased over a period of two hours to reaction temperature. Treatment time was calculated from the point when the temperature was 20°C below the set point. The temperature in the oven was controlled by a Scandia TC 2000 unit, which was supplied with the oven. After the predetermined soak time the oven was shut down and the oven door was opened to allow the reactor to cool naturally. Only one experimental run was performed each day because of the extended heating and cooling times.

2.2.3. Distillation

The three-neck distillation flask still containing the thermally treated, topped tar was removed from the heating vessel. The distillation flask was placed in a heating mantel (see Figure 2-4). The tar was stirred by a propeller at 300 rpm and the temperature was monitored by a thermocouple. To control the rate of heating the current was adjusted by an autotransformer in the range of 0-250 volts. The distillation was performed at a reduced pressure of less than 10 mbars. The vapor outlet from the distillation flask was connected to a short distillation tower of approximately 20 cm. The bottom part of this was filled with iron sponge in order to avoid accidental splashes or foam being carried out together with the vapor. The vapor was condensed in a 50 cm air-cooled tube and collected in a receiver flask (Figure 2-4). Based on prior experience a pitch with a target softening point of 120±10°C was obtained.

2.3. Experimental Results

The produced pitch was subjected to the analyses which are routinely applied to commercial pitch products in the Koppers Denmark laboratory. Softening point, quinoline insoluble, toluene insoluble and coking value were determined using the ISO9000 certified procedures of the Nyborg plant. All results were obtained as an average of two measurements using the methods described in Appendix A and Section 1.1.1. Experimental values are presented graphically, while numerical values are found in Appendix B.

2.3.1. Effect of Treatment Temperature

2.3.1.1 Yields

In the first distillation step 10% or 20% oil was distilled from the tar. The percentage of oil removed in this step influenced the yield after the thermal treatment (Figure 2-7). All yields were calculated as the weight percentage of material on the basis of the feedstock tar. As the treatment temperature was increased, the yield of thermally treated topped tar

was reduced. The loss of material can be regarded as formation of light components (see the GC analysis in Section 5.2). The loss of material could not be entirely attributed to distillation during the treatment. This was further confirmed in the last distillation step where the tar started to distill below the cut-off temperature in the first "topping" distillation.

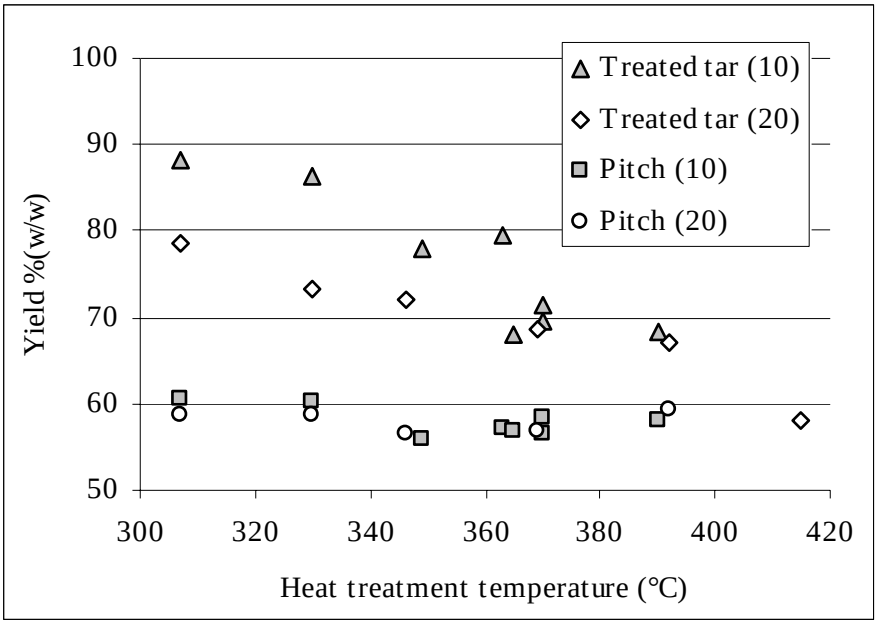


Figure 2-7: Yield after thermal treatment and after the final distillation. In brackets: percentage of oil removed prior to thermal treatment.

The yield of 120±10°C softening point pitch was not affected by the percentage of oil removed by topping before the thermal treatment according to Figure 2-7, but the pitch yield was decreased by including a tar thermal treatment step. At the higher treatment temperatures the yield did show an upturn although it never reached the yield obtained from the untreated tar. This was a rather unexpected finding. On the basis of results with similar thermal treatment of topped coal tar the treatment was expected to increase the pitch yield (Malmros et al., 2000). In Section 2.5.1 where softening point corrected data is presented the tendency is more clearly illustrated. It was not possible to obtain a 120°C softening point from the sample treated at 415°C, because the softening point of the thermally treated topped tar was already 139°C.

2.3.1.2 Analytical

The solvent fractions of the pitch were sensitive to the tar thermal treatment conditions. Figure 2-8 shows an escalating effect on the fraction of TI with increasing thermal treatment temperature. At approximately 370°C there is a notable increase in the formation rate. TI formation does not appear to be sensitive to the amount of oil removed by topping in the first distillation step.

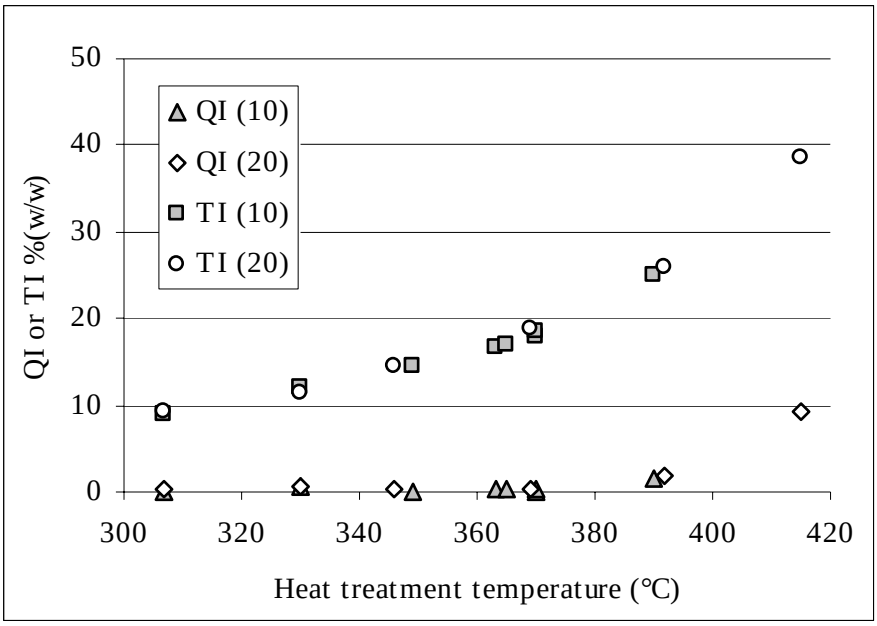


Figure 2-8: Solvent insoluble fractions of the pitch as functions of tar treatment temperature. In brackets: percentage of oil removed prior to thermal treatment.

No QI material was formed at the lower treatment temperatures. The samples which were thermally treated at 390°C and above all contained QI material formed in the pitches. The samples treated at 392°C and 415°C contained mesophase which was visible by optical microscopy (>4μm), so that part of the QI material was found to be mesophase. (See Chapter 4 on the subject of mesophase analysis).

The coking value of the resulting pitch increased when the thermal treatment temperature was increased (Figure 2-9). The increase in coking value did not appear sensitive to the formation of QI material or to the formation of visible mesophase. There are only few plot

points for pitches containing important concentrations of mesophase so their role in the data as a whole cannot be discussed in detail.

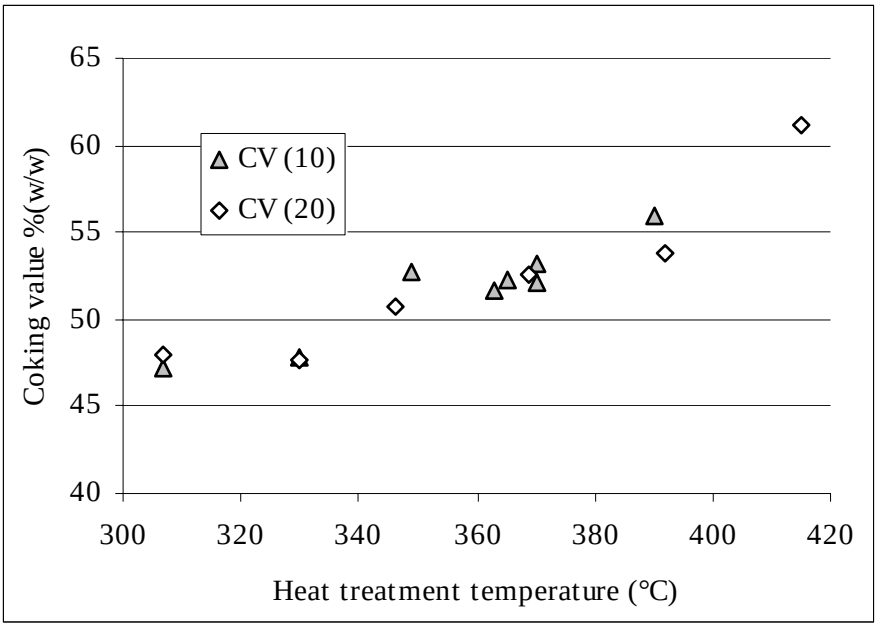


Figure 2-9: Pitch coking values as functions of tar heat treatment temperature. In brackets: percentage of oil removed by topping prior to thermal treatment.

The major finding of this part of the study is that it is possible to increase the coking value of a petroleum pitch by subjecting the precursor material to a thermal treatment. There is a range of operating conditions where the coking value can be increased without the formation of mesophase in the pitch. The unwanted side-effect of this improvement in pitch quality is a reduced pitch yield.

2.3.2. Effect of Soak Time at Constant Temperature

In experiments where the heat treatment temperature was variable and the soak time was constant, it was found that the coking value of a pitch could be increased without creating secondary quinoline insoluble material. Based on this experience a series of experiments at a constant temperature but with varying soak times was carried out. The temperature of 360°C was chosen because this was below the threshold where formation of secondary QI could be expected.

The loss of material during the heat treatment was mainly due to cracking, which leads to the formation of volatile components under reactor conditions. This effect can be seen in Figure 2-10, which shows the yields after each of the manufacturing steps. The resultant pitch yield is sensitive to the duration of thermal treatment (Figure 2-10). The resultant yield of a 120±10°C softening point pitch is reduced for treatment times up to and including two hours. Afterwards the pitch yield reaches an almost constant level. With reference to the previous section, it should be noted that the yield reduction caused by heat treatment is at full effect after around six hours of thermal treatment. It should also be noted that all the experiments are carried out separately and that no material is removed during the treatment, which means that all points are independent of each other. Much of the scatter in the data is due to the pitches not having exactly the same softening point. Section 2.5.2 contains a further discussion about the influence of the softening point.

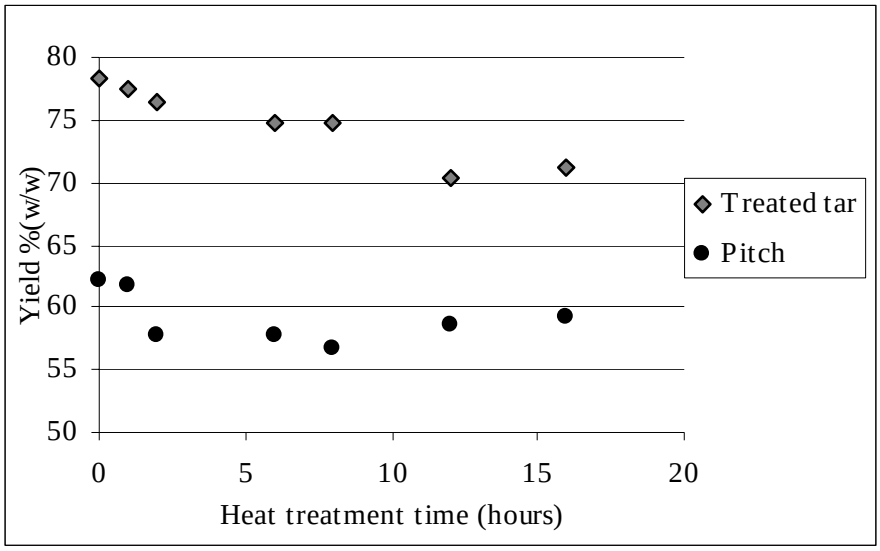


Figure 2-10: Yield of thermally treated topped tar and resultant yield of 120°C SP pitch after thermal treatment at 360°C as functions of soak time.

The results shown as zero hour treatment were obtained from a topped tar stored for two months with other prepared topped tars. This was the maximum storage period for the topped tars. The topped tar was then distilled into a pitch with a softening point of 118.9°C, a pitch yield of 62.2% and a TI of 5.9%. A tar which was distilled directly into

pitch yielded 62.8% of pitch with a TI of 4.6%. The variation was within the experimental uncertainty.

Figure 2-11 shows QI and TI as functions of soak time. Only data from pitches with softening points between 110°-120°C is shown in this figure. During the first two hours of thermal treatment the amount of TI in the resultant pitches increased. Continued heat treatment further increased the TI content, but at a much slower rate. It is important to observe that no QI material was formed at 360°C even with soak times as long as 16 hours. The amount of QI material formed during heat treatment can be seen as an early warning of mesophase formation. Optical microscopy was used to confirm that none of the pitches showed any trace of mesophase.

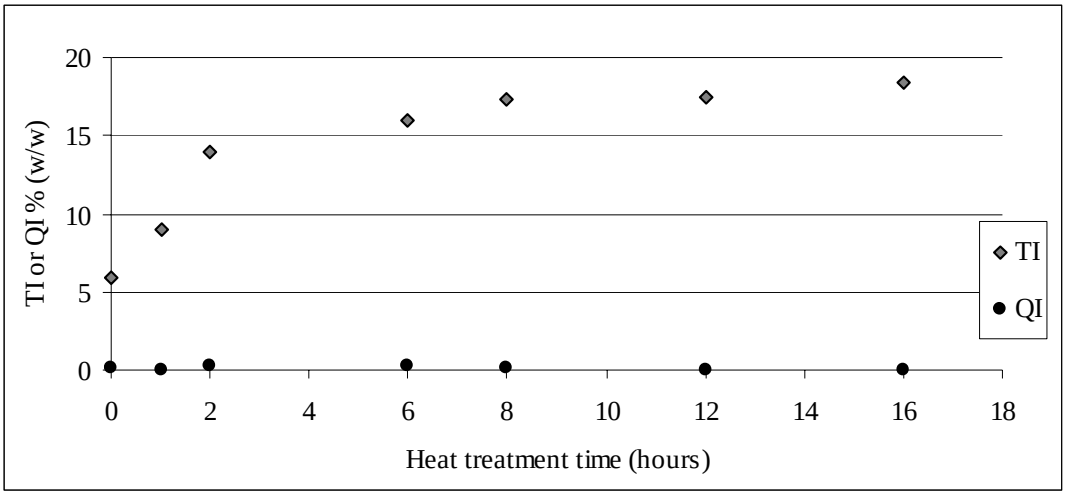


Figure 2-11: QI and TI of pitch as functions of tar soak time of tar thermal treatment at 360 °C.

The measurement of material insoluble in toluene (TI) turned out to be problematic, especially for pitches made from petroleum tar which had not been heat-treated. Apparently, the low content of TI material complicated the filtration. TI values were determined by duplicate testing and the two tests were not allowed to differ by more than 0.5 % absolute to be accepted. It was not possible to follow this procedure in the analysis of the low TI pitches. Changes to the analytical procedure in order to obtain more precise data were considered. A possibility might be to add diatomaceous earth filtering aid to the

toluene solution before filtration. It was, however, chosen to regard the analysis method as a standard used for all pitches even though it was only intended for coal tar pitch. A modified TI method would lack a wider range of credibility because the TI value is an empirical pitch quality parameter anyway.

The coking value of the pitch was improved by the low-temperature thermal treatment. The main increase took place within the first two hours of treatment (Figure 2-12). After this initial increase the coking value stabilized at a constant level. This analysis turned out to be very sensitive to softening point (the SP corrected values are given in Section 2.5.2)

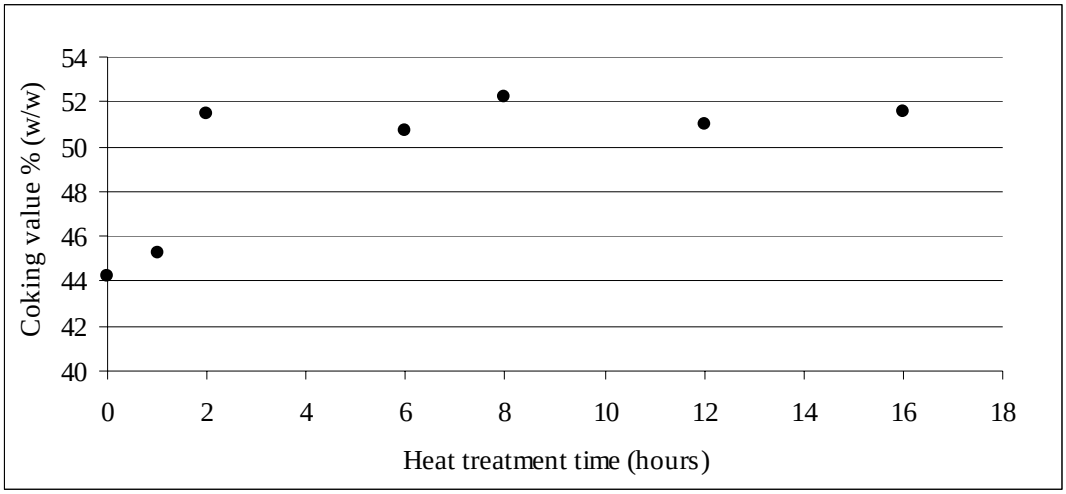


Figure 2-12: Coking value of pitch as function of tar soak time of tar thermal treatment at 360 °C.

2.3.3. Influence of Precursor Material Origin and Constitution

In the following section experiments on combined coal and petroleum material are described. The presented results are obtained experimentally without further calculations. The two feedstocks for the experiments were received separately as topped tars from the industrial plant (F98017A and F98020, Table 2-1). Three mixtures were made from the two samples: 50/50, 80/20 and 90/10 (weight of topped coal tar/weight of topped petroleum tar). All three mixtures and the two pure topped tars were heat-treated for six hours at four temperatures: 350°C, 370°C, 385°C and 410°C (see experimental plan in

Table 2-2). The heat-treated samples were distilled into a pitch with a target softening point of 120°C.

Coal/petroleum	350°C	370°C	385°C	410°C
0/100	x	x	x	x
50/50	x	x	x	x
80/20	x	x	x	x
90/10	x	x	x	x
100/0	x	x	x	x

Table 2-2: Experimental plan for thermal treatment of blended tars.

The pitch yields are illustrated in Figure 2-13 as functions of the content of topped coal tar in the mixture. The pitch yield obtained by simply distilling the tar into pitch without initial treatment is depicted as the data with legend “None” in the figure. The pitch yield from petroleum tar was reduced by the thermal tar treatment. This result was in agreement with earlier results (Figure 2-7 and Figure 2-10). The pitch yield from 100 % coal tar was increased with increasing treatment temperature. This finding was in accordance with the results found by Malmros et al., 2000, who also reported increasing yield with increasing severity of the thermal treatment of topped tar. The pitch yield from blended materials generally increased with increasing tar thermal treatment temperature.

The yield of directly distilled pitch decreased with increasing amounts of coal-derived material in the pitch, but the thermal treatment was capable of reversing this tendency. The topped tar treated at temperatures between 350°C and 385°C seems to give more or less the same pitch yield regardless of the initial composition. Clearly, the two materials react very differently to thermal treatment. Further conclusions (especially concerning the treatment at 410°C) are complicated by the fact that the yield is strongly affected by how close the measured softening point is to the target after the final distillation step (see further discussion in Section 2.5.3).

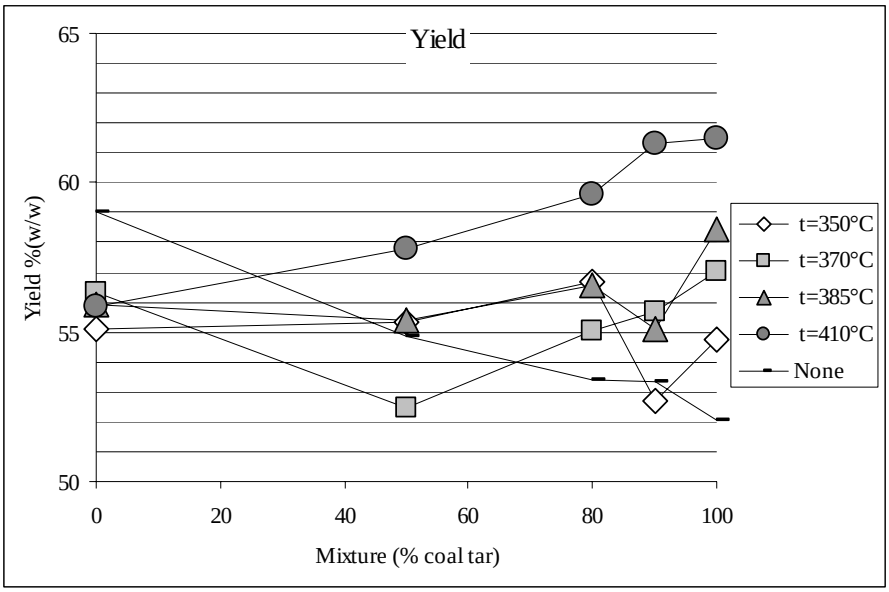


Figure 2-13: Pitch yield from heat-treated tar as a function of topped coal tar in the blend prior to the thermal treatment. The treatment temperature is given in the legend, "none" refers to straight distilled pitch.

Figure 2-14 shows the TI of the resultant pitches as a function of the content of coal tar material in the topped tar. Tar thermal treatment increases the TI of the final pitch. The material derived from petroleum tar is more sensitive to thermal treatment than the coal tar material, most likely because the thermal history of this material is less severe than the production of coal tar.

Figure 2-15 shows the content of QI in the pitch. It should be noted that only the treatment at 410°C increases the quinoline insoluble fraction. This is important because it proves that tar treatment at 385°C and below does not cause formation of mesophase.

Secondary QI is defined as the part of the QI which is formed during the heat treatment of the tar. For the pure petroleum pitches all the QI in the pitch can be interpreted as secondary QI because there is hardly any QI in the original petroleum tar. The coal tar pitches and the blends contain natural QI from the coal tar. The amount of secondary QI in these samples can be calculated from Equation 2-1.

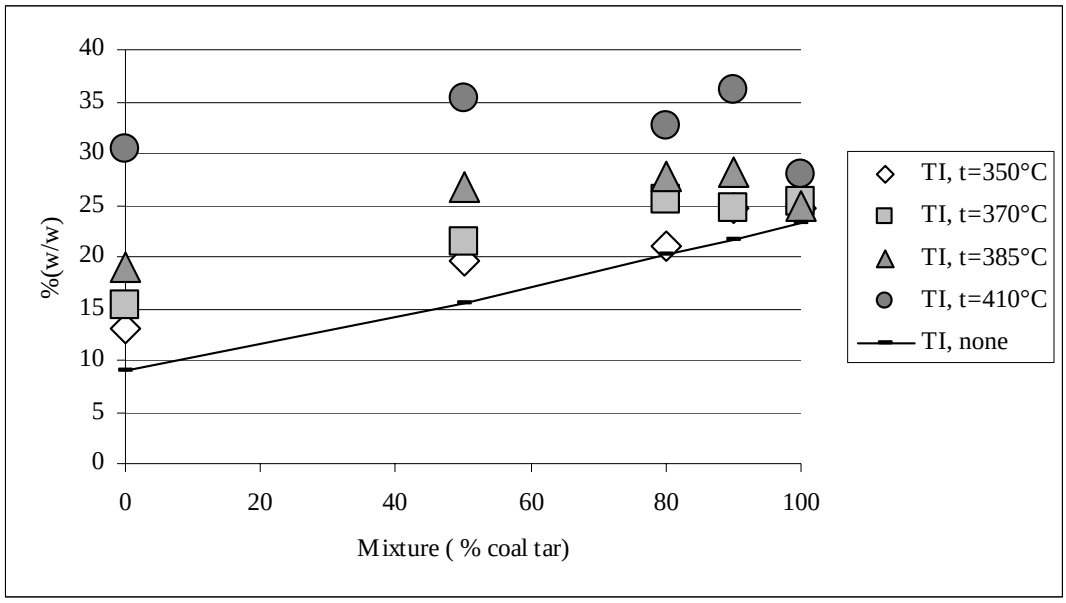


Figure 2-14: Toluene insoluble content as a function of topped coal tar in the blend prior to the thermal treatment. The treatment temperature is given in the legend, “none” refers to pitch straight distilled pitch.

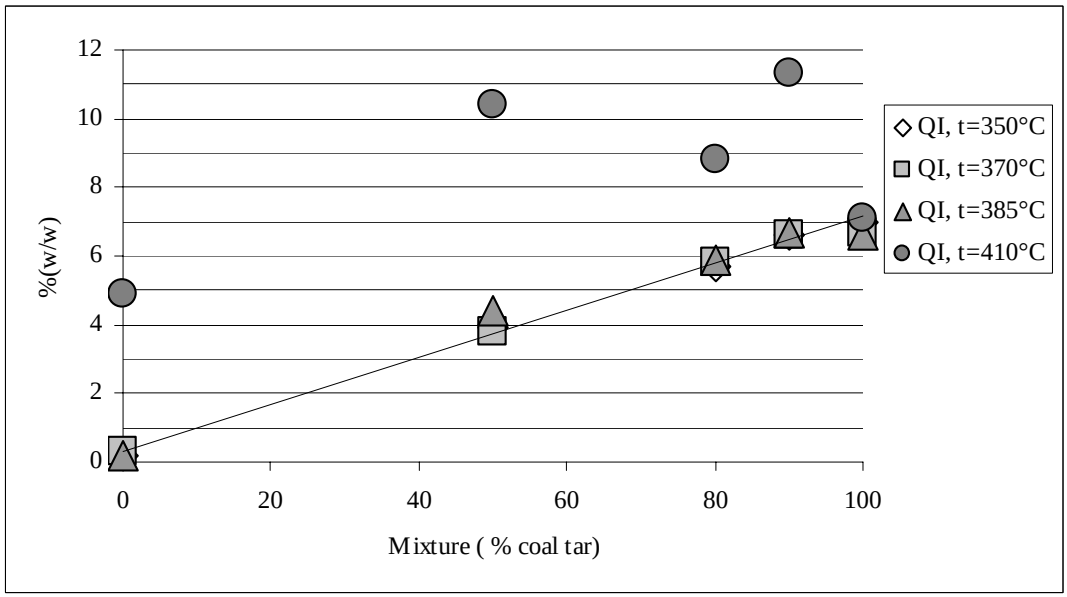


Figure 2-15: Quinoline insoluble content as a function of topped coal tar in the blend prior to the thermal treatment. The regression line for the data thermally treated at 350°C is included.

$$\text{sec.QI} = \text{QI}_{\text{pitch}} - \text{QI}_{\text{top.tar}} \frac{\text{yield}_{\text{top}}}{\text{yield}_{\text{pitch}}} \text{X}_{\text{TCT}} \qquad \text{Equation 2-1}$$

sec. QI	Secondary quinoline insoluble of pitch
QI_{pitch}	Quinoline insoluble of pitch
$QI_{top\ tar}$	Quinoline insoluble of topped coal tar
$yield_{top}$	Yield of topped tar relative to tar
$yield_{pitch}$	Yield of pitch relative to tar
X_{TCT}	Fraction of topped coal tar in the topped mixed origin tar

In Figure 2-16 the secondary quinoline insoluble content is shown for the different temperatures and tar ratios. Once again it should be noted that heat treating the topped tars at 385°C and lower temperatures does not propagate the formation of components insoluble in quinoline. In the pitches which contain petroleum derived material and have been tar-treated at 410°C approximately 5% secondary QI has been formed. It seems the coal tar pitch is less sensitive to thermal treatment than the other materials. This effect may, however, be a result of the fact that this particular sample has a lower softening point than the others. In Figure 2-17 the calculated content of secondary QI is plotted as a function of the pitch softening point without any consideration of the tar origin, and there seems to be log-linear relationship between the two properties.

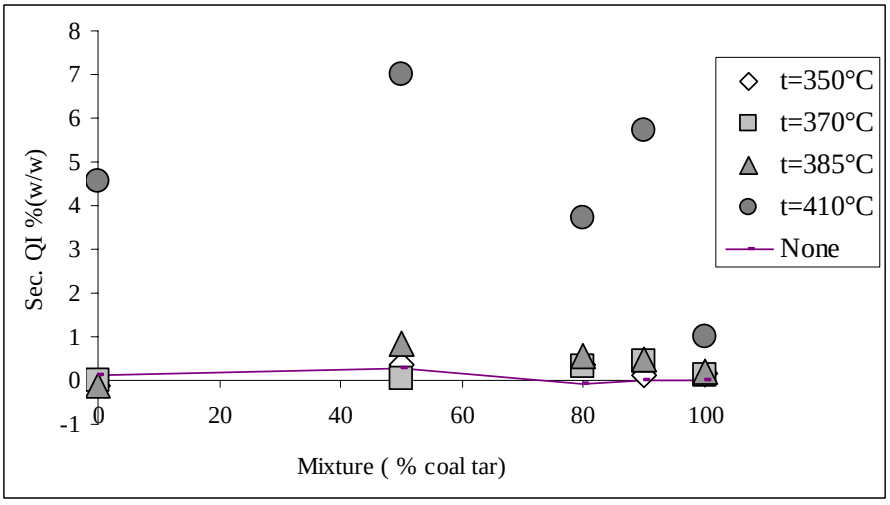


Figure 2-16: Secondary QI (Equation 2-1) as a function of topped coal tar in the blend prior to the thermal treatment.

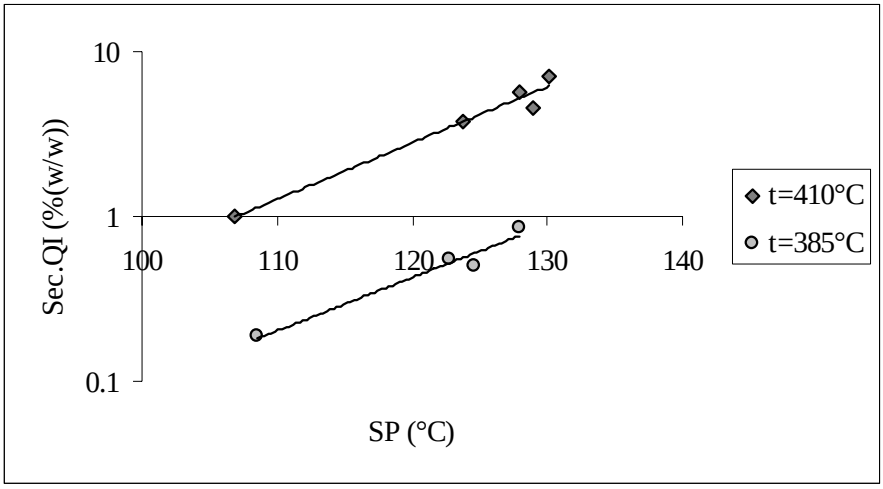


Figure 2-17: Secondary QI as a function of the pitch softening point.

The coking value of the pitch is improved by increasing the temperature of the tar thermal treatment (see Figure 2-18). Unfortunately, this measurement is particularly sensitive to the closeness of the softening point to the target. The severity of this problem is indicated by the false impression that the pitch coking value has decreased with increasing tar thermal treatment temperature for the 100% coal tar pitch. This result is not in accordance with earlier findings (Malmros et al., 2000) and it is further analyzed in Section 2.5.3.

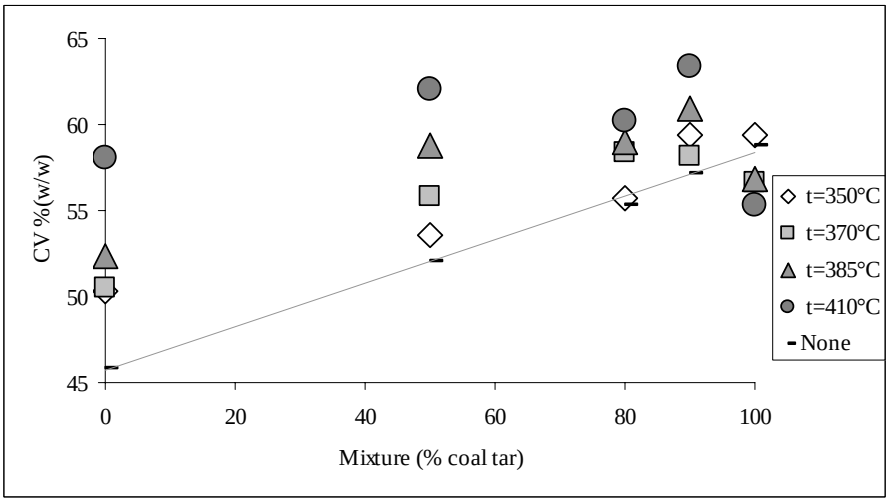


Figure 2-18: Coking value of combined tars as a function of topped coal tar in the blend prior to the thermal treatment.

2.4. Methods for Correcting the Analytical Result to a Common Basis

The thermally treated topped tars were distilled into pitch with a target softening point of 120°C. This was typically obtained with a precision of ±10° (Appendix B) with the exception of the topped coal tar pitch treated at 385°C and 410°C, which differed by up to 15°C. The precision with which the softening point was reached turned out to have a large effect on analytical data obtained for the pitch. It was considered simply to repeat all the experiments and in this way reach the softening point with a better precision. This idea was discarded for two reasons. First of all, it was only possible to run an average of four experiments a week because the autoclave had to cool down completely before it was possible to handle it again. Secondly, even if all experiments were repeated the softening points would still deviate from 120°C and the scatter would still not be completely removed.

A second possibility was to perform the distillation in steps and measure the softening point at every break in the distillation. This possibility was also discarded because the pitch would have to cool to below 250°C before it would be safe to sample it. A softening point measurement takes at least 15 minutes and with the heating and cooling of the sample this would take a lot of time. Removing several samples would also introduce more weighting errors, which would compromise the pitch yield data.

The uncertainty in the measured properties derived from the final distillation was due to the influence of the amount of oil removed from the samples. If it is assumed that the properties are mainly influenced by high-boiling components, the volatile components have a “constant” influence. It might then be possible to correct the data to a specific softening point by applying general knowledge of the influence of the softening point on the properties. Following this idea, experiments with distillation of the untreated topped tars were conducted in order to find the influence of the softening point on the measured properties.

The topped tar or topped tar blends were transferred to a one-liter distillation flask and the distillation was performed with the equipment shown in Figure 2-4. The distillation was

interrupted and the material was allowed to cool to below 250°C for a sample to be taken for analysis. Both sample and distillate were weighed for later calculation of pitch yield and the distillation was continued until data was obtained in the target softening point range. Softening point, TI, QI and coking value were measured on the samples. The data obtained from the experiments is listed in Appendix C. In Figures 2-19 to 2-21 the data is depicted graphically.

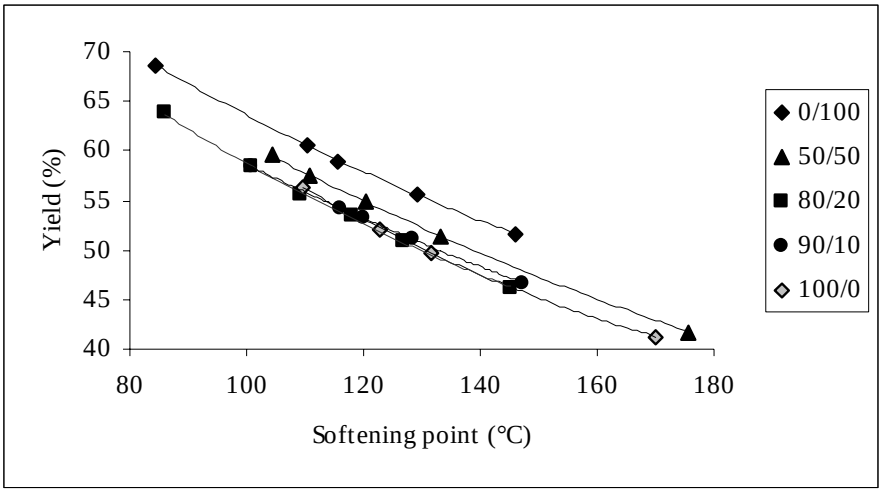


Figure 2-19: Straight distilled pitch yield as a function of softening point. Legend: Percentage of topped coal tar /topped petroleum tar.

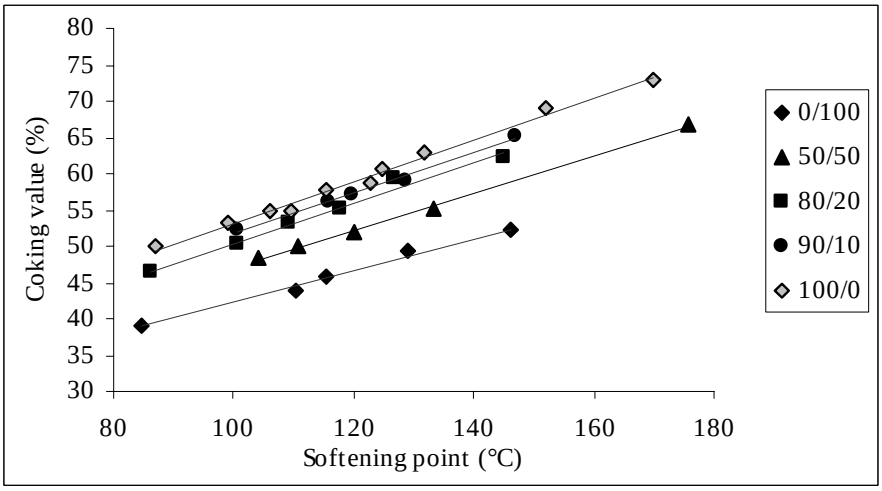


Figure 2-20: Coking value (CV) of straight distilled pitch as a function of softening point. Legend: Percentage of topped coal tar /topped petroleum tar.

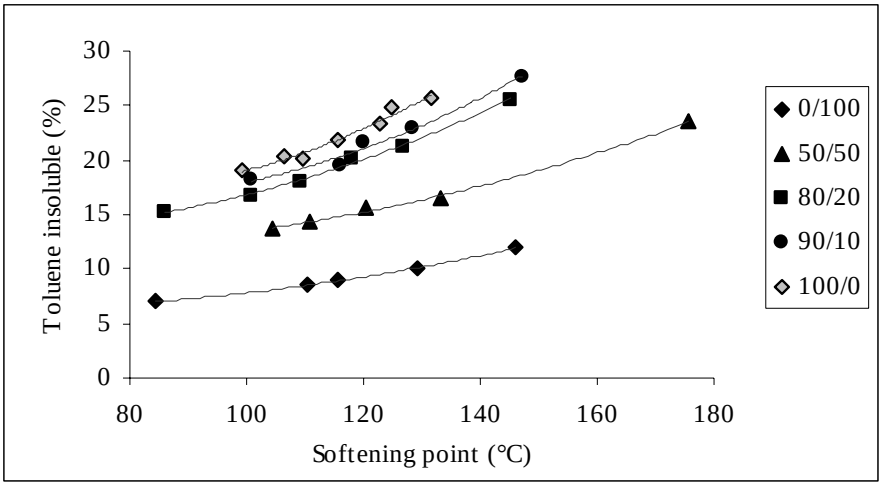


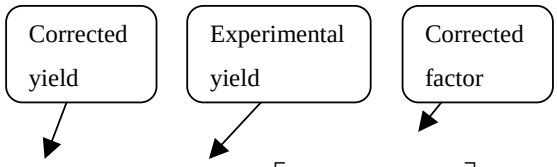
Figure 2-21: Toluene insoluble (TI) of straight distilled pitch as a function of softening point. Legend: Percentage of topped coal tar /topped petroleum tar.

The data was fitted by second-degree polynomials as shown in Figures 2-19 to 2-21. The coefficients to Equation 2-2 are given in Appendix C. It was found that the coking value was best fitted by a linear regression.

$$Y(SP) = a * SP^2 + b * SP + c \qquad \text{Equation 2-2}$$

Y(SP)	Calculated response (yield, coking value or toluene insoluble)
a, b, c	Fitted coefficients
SP	Softening point

With the aid of Equation 2-2 a method for correcting yield, TI and CV to a given standard softening was found. As stated earlier, the aim of the correction is to remove the uncertainty of the data derived from the final distillation step. Equation 2-3 demonstrates the correction for the yield. The actual, experimental pitch yield was multiplied by a correction factor. This factor was found by taking the yield of straight distilled pitch at the reference softening point (Equation 2-2 with $SP=SP_{ref}$) and dividing it by the yield of straight distilled pitch with the softening point which was actually obtained for the thermally treated pitch (Equation 2-2 with $SP=SP_{exp}$). Similar functions were constructed for TI, and the CV is shown in Appendix C.



$$\text{Yield}(SP_{ref}) = \text{Yield}_{exp}\left[\frac{\text{Yield}_{SD}(SP_{ref})}{\text{Yield}_{SD}(SP_{exp})}\right] \qquad \text{Equation 2-3}$$

$\text{Yield}(SP_{ref})$ Yield corrected to a reference softening point (i.e. SP_{ref}=120°C)

Yield_{exp} The pitch yield found experimentally for the tar-treated pitch

$\text{Yield}_{SD}(SP)$ Yield of straight distilled pitch with the softening point SP (Equation 2-2)

SP_{ref} Reference softening point (i.e. SP_{ref}=120°C)

SP_{exp} The softening point found experimentally for the tar-treated pitch

2.5. Corrected Analytical Results

The equations given in Section 2.4 were used to correct the tar thermal treatment results. The treated results are graphically presented in this section and the data is listed in Appendix D.

2.5.1. Effect of Treatment Temperature

The yields were corrected to softening points of 110°C and 120°C by use of Equation 2-3. The results are shown in Figure 2-22. The correction clarifies the tendencies in the data so that it becomes clearer that there is first a decrease in yield followed by an increase.

The magnitude of the decrease in yield was calculated by Equation 2-4. The calculated yield decrease has a maximum of approximately 6% at a temperature close to 360°C (Figure 2-23).

$$\text{Yield decrease} = \text{Yield}_{SD}(SP_{exp}) - \text{Yield}_{exp} \qquad \text{Equation 2-4}$$

Yield_{exp} The pitch yield found experimentally for the tar-treated pitch

$\text{Yield}_{SD}(SP)$ Yield of straight distilled pitch with the softening point SP (Equation 2-2)

SP_{exp} The softening point found experimentally for the tar-treated pitch

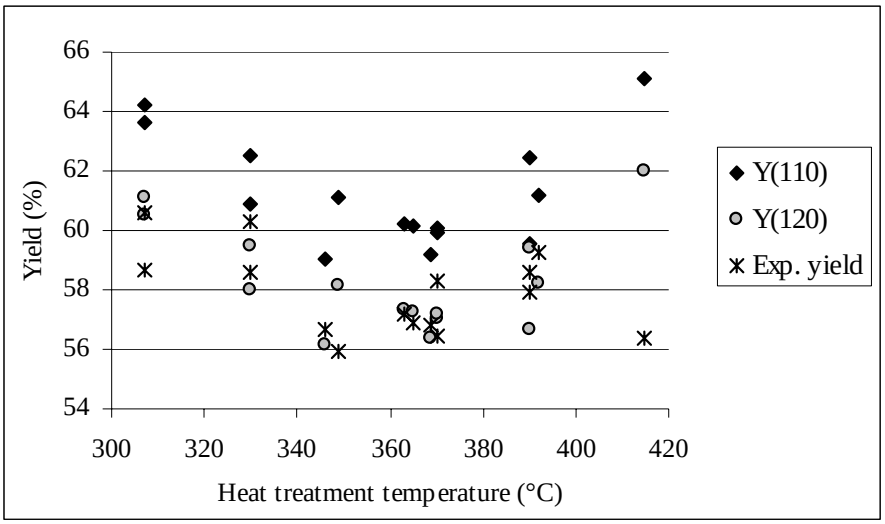


Figure 2-22: Pitch yield from tar thermal treatment corrected to softening points of 110°C and 120°C.

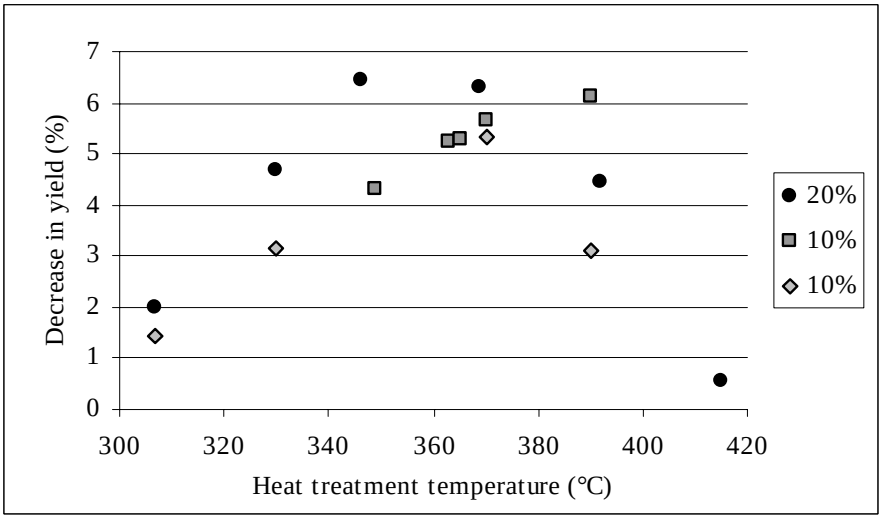


Figure 2-23: Decrease in yield calculated by Equation 2-4 as a function of thermal treatment temperature. The legend shows the amount of oil which was removed from the tar prior to thermal treatment in three independent distillations.

In Figure 2-24 corrected coking values are shown as functions of the heat treatment temperature. It is seen that the experimental values are generally very similar to the values found at SP=120°C. The correction produces a linear relationship with respect to thermal treatment temperature.

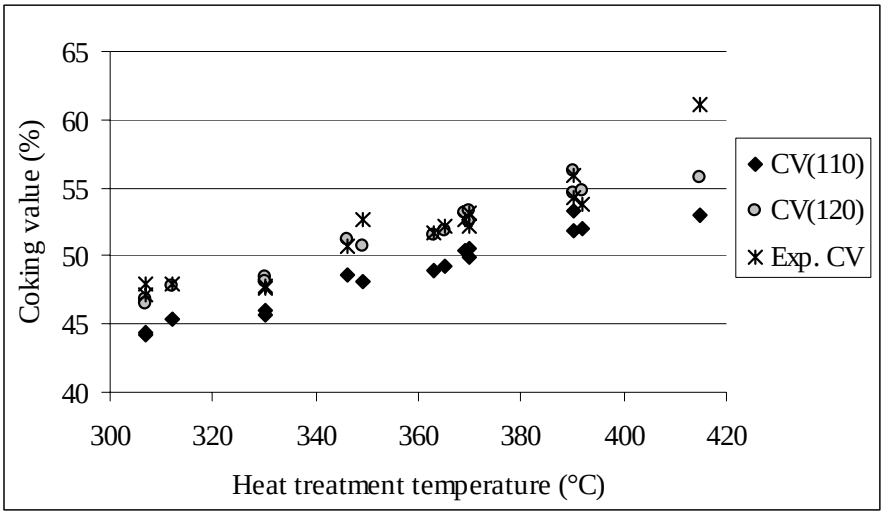


Figure 2-24: Coking values corrected to softening points of 110°C and 120°C as functions of thermal treatment temperature.

2.5.2. Effect of Soak Time at Constant Temperature

Both the yield and the coking values showed a large scatter in the data series with a constant soak temperature of 360°C (see Figure 2-12 and 2-13). In Figure 2-25 the yield corrected to pitch with softening points of 110°C and 120°C is depicted as a function of soak time. The correction of the data underlines the effect of soak time and allows the inclusion of two data sets which were first discarded because the softening point was outside the defined boundaries. The pitch yield first decreased with increasing soak time. After a two hour treatment no further decrease of yield was observed for the resulting pitch. The 16-hour treatment seemed to increase the pitch yield again but since this observation is based on one point it is insufficient to draw any definitive conclusions. If the effect was genuine it could be interpreted as a warning of mesophase formation. The average pitch yield from two to 12 hours' heat treatment is calculated to be 60% for a 110°C softening point pitch and 57% for a 120°C softening point pitch.

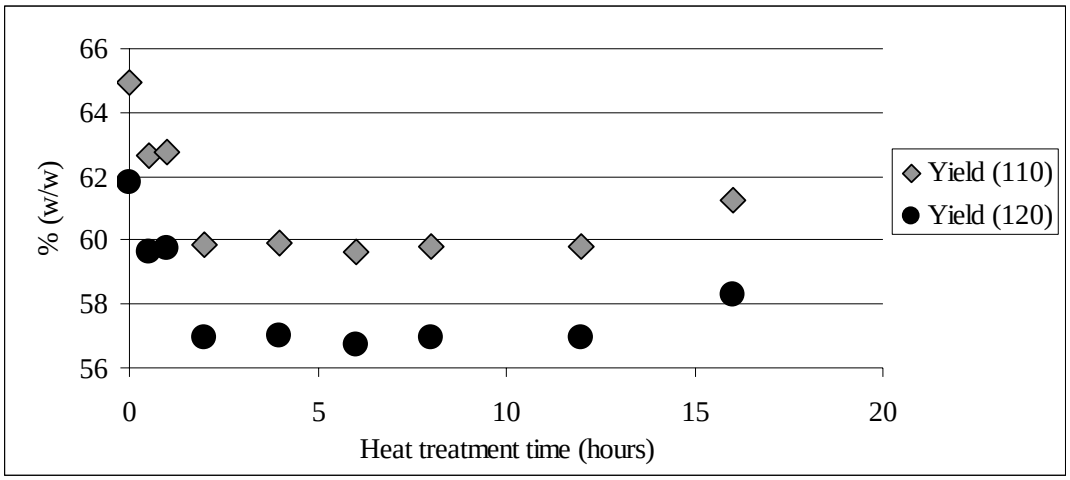


Figure 2-25: Corrected yields (Equation 2-3) of pitch produced, including a tar thermal treatment at 360°C, as functions of soak time.

In Figure 2-26 the corrected coking values are shown as functions of the time used for heat soaking the topped tar. As seen for the yield the correction allows data sets which were ruled out because they were not within the original softening point range criteria. The coking value stabilizes at 49.5% in a 110°C softening point pitch or at 52.2% in a 120°C softening point pitch.

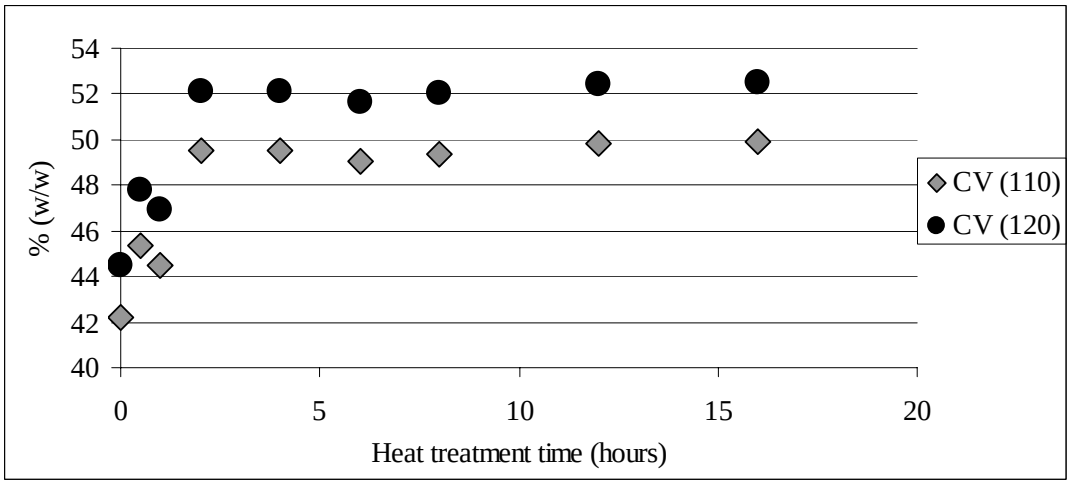


Figure 2-26: Corrected coking values of pitch produced, including a tar thermal treatment at 360°C, as functions of soak time.

2.5.3. Effect and Interaction of Precursor Material

The pitch yields of the thermally treated blends are shown in Figure 2-27. Unlike the results for the data series concerning the effect of soak time the correction does not simplify the conclusions from the data. The straight distilled yield of petroleum pitch is higher than the yield obtained from the coal tar pitch. The two materials react differently to the tar thermal treatment process, resulting in almost the same pitch yields at the lower treatment temperatures. The blended topped tars containing 10 and 20 % topped petroleum tar react in the same way as the pure coal tar with respect to pitch yield, while the 50/50 blend gives a reduced pitch yield at the low temperatures of 350°C and 370°C followed by an increase.

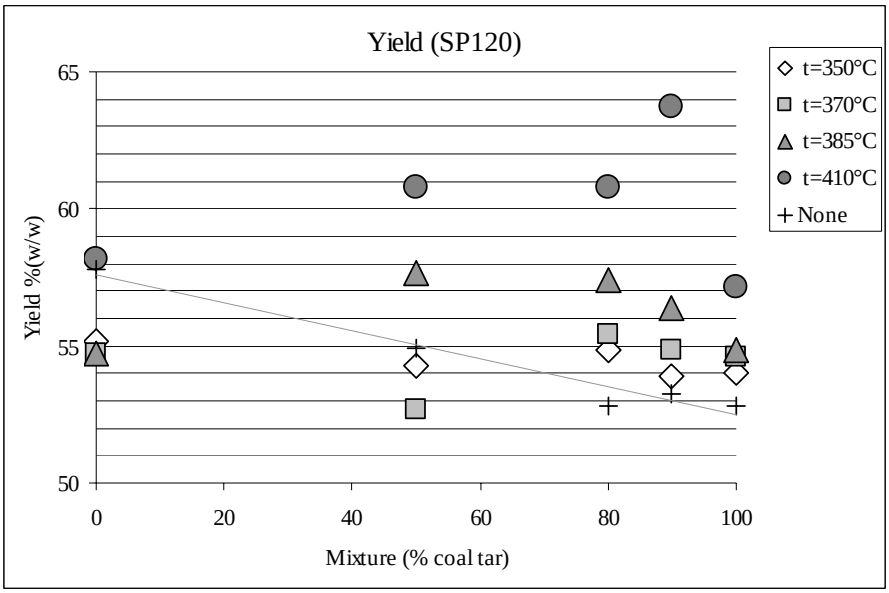


Figure 2-27: Pitch yield corrected to a softening point of 120°C (Equation 2-3) as a function of topped coal tar in the blend prior to the thermal treatment. The treatment temperature is given in the legend, “none” refers to straight distilled pitch.

There seems to be some interaction between the two feedstocks, but because the correction clearly does not account for all the data scatter in this case, it would not be safe to draw further conclusions. This caution is justified by the fact that the calculation of the straight distilled yields does not fall on a line. This indicates that there might be more variation in the determination of the straight distilled yields, which were determined by weighing the

distillate fraction instead of the residue fraction (see Section 2.4 for further details). This procedure does not take into account material which might be lost in the vacuum pump and elsewhere in the equipment or lost as non-condensable volatile. This small but variable source of error might have partly negated the correction procedure. Such an error would not affect the determination of CV and TI. It would also not affect the correction of the earlier results (Sections 2.5.1 and 2.5.2) critically since they are only based on one tar material.

The uncorrected experimental coking values for the coal tar pitch indicated that there might be a decrease in coking value as a result of tar thermal treatment (Figure 2-18), but this is difficult to explain from practical experience. The correction term reversed this unexpected tendency in the data and turned it into a small increase. Correction of the coking value (Figure 2-28) and the toluene insoluble (Figure 2-29) to a standard softening point removes some of the scatter seen in this data. At the same time it also removes the indication of interaction between coal- and petroleum-derived materials, so this suggestion is unproven. There is less potential for tar thermal treatment to improve mixtures containing a high proportion of coal tar, or indeed the 100% coal tar material, so improvements have to be considered with this fact in mind.

2.6. Discussion of Tar Thermal Treatment

The effect of tar thermal treatment on petroleum-derived pitch has been investigated. It was found that the coking value and the toluene insoluble fraction can be increased without causing mesophase formation in the resulting pitch. Experimental results published by Azami et al., 1994, showed that a certain period of time was needed before formation of mesophase. Since the present study was conducted at much lower temperatures, it is impossible to state that mesophase would have appeared if the treatment had been extended.

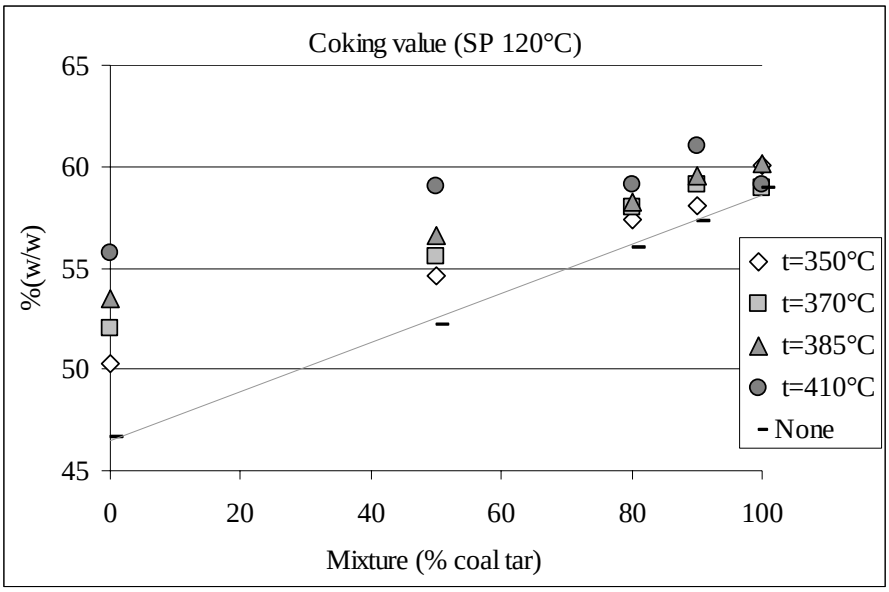


Figure 2-28: Coking values corrected to a pitch softening point of 120°C as functions of topped coal tar in the blend prior to the thermal treatment. The treatment temperature is given in the legend, “none” refers to straight distilled pitch.

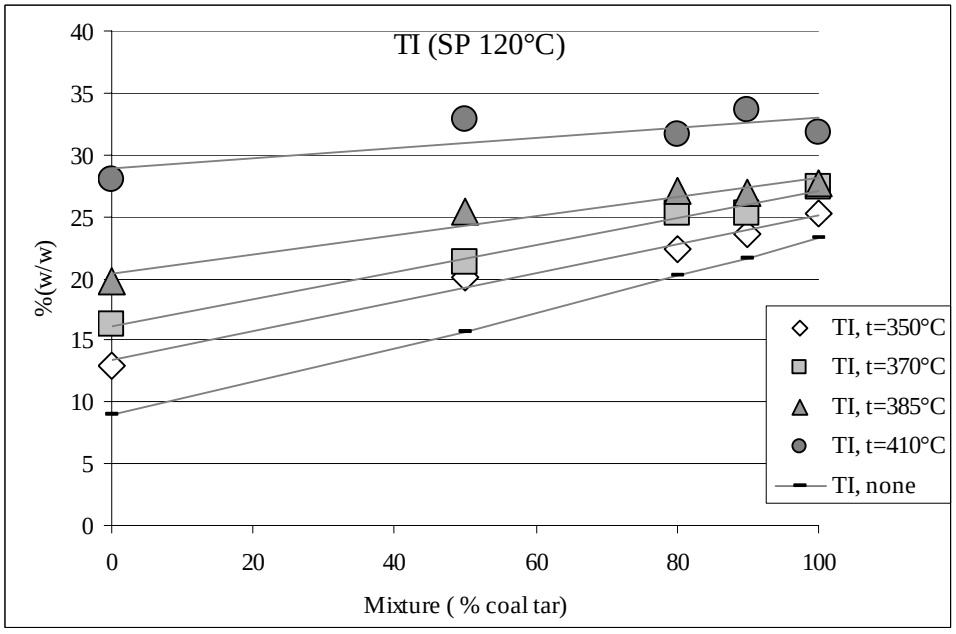


Figure 2-29: Toluene insoluble corrected to a pitch softening point of 120°C as a function of topped coal tar in the blend prior to the thermal treatment. The treatment temperature is given in the legend, “none” refers to straight distilled pitch.

Based on the results from the present study for petroleum material and the results found in the literature for coal tar material, the temperature range of 380°C to 390°C seems to be significant with respect to controlling the outcome of the thermal treatments. Malmros et al., 2000, point out that a particular modification to the pitch can be obtained either by relatively long soak time/low temperature or by short soak time at high temperature. This theory is supported by several studies (Koštál et al., 1994, Py et al., 2000), which show that TI follows simple first or second order reaction kinetics. However, neither the equipment used in this study nor industrial scale pitch production plants are designed for short soak time, high-temperature treatments, so 390°C seems to be the practical temperature maximum for thermal treatments.

In the series concerning the effect of soak time on the pitch properties, it was found that the first two hours of treatment have by far the largest impact on all measured properties. In fact, neither the yield nor the coking value was significantly increased by prolonged treatment. This outcome is not in accordance with other literature on temperature/soak time interdependence. A review of the experimental data points of Koštál et al., 1994, shows that TI and QI increase at the beginning of the experiments. This might indicate an unrecognized mechanism active in the early phases of the treatment.

The experiments on pure coal tar and petroleum tar confirm that the petroleum material is much more sensitive to thermal treatment than the coal tar material. The main difference between the two is that the yield of petroleum pitch is lowered by thermal treatment while the opposite is seen for coal tar. The increase in TI and CV is greater for the petroleum pitch. These differences most likely derive from the different thermal history of the two materials. There is more potential for improvement in the petroleum material because some tar heat treatment actually took place when the coal tar was created in the coking oven.

When the study was initiated it was expected to see a clear interaction between the coal tar and the petroleum tar during the treatment. This was based on the difference in hydrogen content of the two materials, which could give rise to a hydrogen donor/acceptor effect. A review of literature sources (Wombles et al., 2000, and Pérez et al., 2000) supported this

expectation. It was, moreover, expected that this would result in a strong non-linearity of the measured properties with respect to percentage of coal tar material in the feed. However, once the data had been corrected to a standard reference softening point it was not possible to conclude that there was any interaction.

The missing effect might be explained in two ways. The first rather negative explanation could be that the experiments are simply not sensitive enough to pick up any fine interaction effects. This might very well be true but any effect below the present sensitivity level would not be of much interest from a practical point of view.

The second more likely explanation is that the experiments were simply not carried out at a sufficiently high temperature for the mixing effects to have any real influence. In the paper of Granda et al., 2000, the effect was first realized in connection with mesophase formation. Likewise, Wombles et al., 2000, concluded that incorporation of 15% petroleum-derived material in binder pitch does not significantly change the properties of aluminum smelting anodes made from this mixture in comparison with anodes made from pure coal tar pitch. In these cases the positive interaction effects are seen in connection with the actual carbonization of the pitch.

The fact that no clear interaction effect between coal tar and petroleum materials is seen indicates that there are no practical reasons for not treating the materials separately. This result is of great practical importance because there are practical benefits of keeping the oils from coal tar and petroleum tar separate. Separate thermal treatment would also make it possible to treat only one of the materials. This would make it possible to keep the well-proven quality of the coal tar pitch and combine it with a petroleum material whose coking value was improved by the thermal treatment.

2.7. Short Conclusion

The conclusions to be drawn on the basis of the thermal treatment experiments are the following:

1) Pitch properties can be altered by careful thermal treatment.
2) The treatment temperature should for practical reasons be kept below 390°C.
3) The effect of soak time is greatest within the first two hours of treatment.
4) There is no significant interaction between coal tar and petroleum tar in the temperature range studied.

3. Size Exclusion Chromatography

The main aim of this study has been to investigate the influence of mild thermal treatment on a pitch precursor tar. The results presented in Chapter 2 show that it is possible to modify the analytical profile of a pitch. The nature of the modifications, especially on the molecules which remain in the pitch, is, however, still not very well understood. The complexity of the material makes it difficult to access information about the fate of specific molecular species. There is, moreover, a serious lack of more fundamental understanding. Thermal treatment was expected to result in loss of side chains and polymerization into large molecules eventually becoming mesogens, but it is difficult to analyze these components.

Size exclusion chromatography (SEC) has proven to be a very powerful tool to obtain molecular weight distribution in the polymer science (Yost et al. 1980). It has also been applied to characterization of coal tar pitches (Mulligan et al., 1987, Lazaro et al., 1999, Boenigk et al., 1990), other coal-derived material (Johnson et al., 1997, Lafleur et al., 1989) and aromatic petroleum products (Brulé et al., 1980). The goal of applying SEC to pitches produced from thermally treated precursor material has been to be able to pinpoint the molecular classes formed during mild thermal treatment.

3.1. Principles of Size Exclusion Chromatography

The principle of size exclusion chromatography differs from other chromatographic systems by the mechanism by which the components are separated. In normal liquid chromatography the molecules are separated by their affinity for mobile phase (liquid) and stationary phase (solid). In a perfect SEC analysis the compounds are not adsorbed onto the stationary phase, the components of the sample are separated by their ability to enter pores in gel particles. Larger compounds which cannot enter the pores will travel with high linear velocity in the space between the gel particles and therefore be first eluted. Smaller components will enter pores which are larger than they are (or more precisely larger than their hydrodynamic volume) and thus be delayed (Figure 3-1).

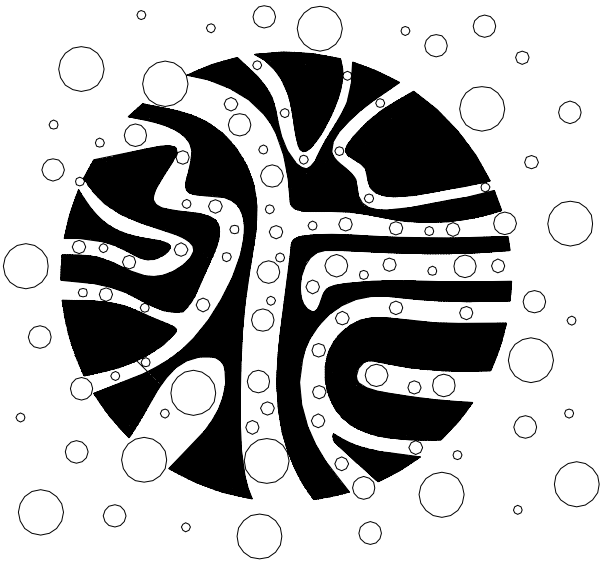


Figure 3-1: Separation by molecular size in a gel particle (inspired by Yost et al., 1980).

An idealized SEC calibration curve is shown in Figure 3-2 where a SEC chromatogram of the four components A, B, C and D is depicted. The SEC columns are packed with particles of a porous gel as the one illustrated in Figure 3-1. Component A is too large to enter any of the pores and will therefore travel with high linear velocity in the interspaces between the gel particles. The elution volume of this first component is referred to as the total exclusion limit of the chromatographic system. Components B and C are progressively smaller and can enter some pores and will thus be eluted in the size exclusion zone. Components of the same or smaller hydrodynamic volumes than the mobile phase (component D) will enter all pores and suffer the longest delays. They will be eluted with the original sample solvent. In perfect SEC no components will be eluted after this total permeation limit of the system. In theory, the retention time is proportional to the logarithm of the molecular weight.

A chromatographic system consists of both a solid stationary phase and a liquid mobile phase. Normally, the stationary phase plays the most active role, but in SEC it is the liquid phase which has the largest influence on the success of the separation. In many size exclusion chromatographic systems, compounds which are known to be found in pitch will be eluted after the permeation limit and they might additionally be grouped by chemical

functionality. These effects are caused by absorption to the column packing. The phenomenon is referred to as non-size retention or non-size effects.

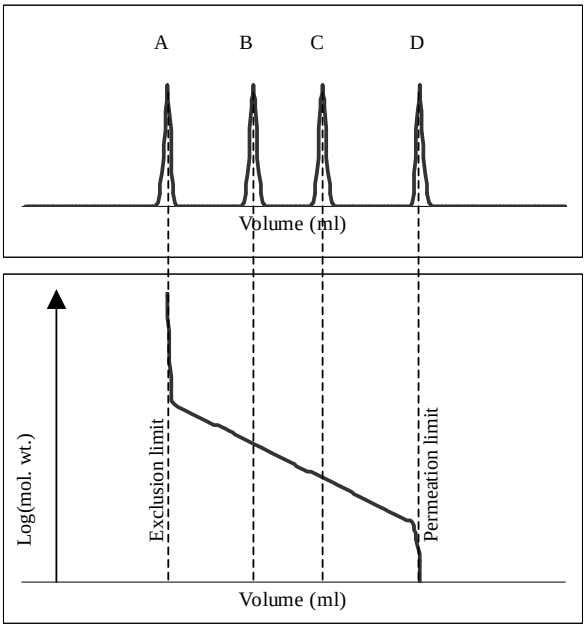


Figure 3-2: Idealized calibration curve (bottom) based on the calibration standard samples A, B, C and D (inspired by Yost et al., 1980).

In the choice of chromatographic system and operating conditions there are two major concerns to be taken into account:

1. Solubility of the sample in the mobile phase
2. Non-size effects

The sample is transported into the column dissolved in the liquid mobile phase. For this reason only the part of the sample which is soluble in the mobile phase can be analyzed. Ideally, the mobile phase should be a very good solvent for the sample. If the sample is only partially soluble, this can introduce non-size effects which might multiply because of high column pressure. These unwanted effects can be reduced by 1) choosing another solvent and 2) raising the column temperature (Yost et al., 1980).

3.2. Literature Study

SEC was first applied to polymers to obtain molecular weight distributions. It was working almost according to the theory due to the fact that a polymer sample typically consists of very similar molecules. All the molecules are built up from the same monomer so there is an intuitive relationship between size and molecular weight. When we work with the types of samples which are relevant here it might not be possible to obtain a true calibration curve. Actually, the first step has been backwards to gain confidence that the method will yield information about the samples. In this subject area there are more articles about calibration and validation of the method than articles where the method has actually been used for solution of practical problems.

3.2.1. Calibration and Validation

An important question when SEC is applied to petroleum- or coal-derived samples is whether it can be assumed that a molecular weight distribution curve has been obtained. One approach has been to test this by pure compounds which are known to appear in coal or petroleum-derived samples. This approach has been based on dimethylformamide (Mulligan et al., 1987) and dichloromethane (Lafleur et al., 1989) as mobile phases. By use of these two solvents it was found that

1. The components molecular weight could not be represented by a log-linear function of elution volume
2. Some components were eluted after the permeation limit
3. Components seemed to be divided into groups of functionality

These are typical indications of non-size effects. Better results were obtained by Lafleur et al., 1989, using N-methyl-2-pyrrolidinone (NMP) as mobile phase. They found that most PAH were separated by a size exclusion mechanism. Cataannelated, unsubstituted PAH (naphthalene, anthracene and similar) and azaarenes (derivates of pyridine, indole, quinoline and other) gave retention volumes close to the polystyrene calibration curve. Pericondensed, unsubstituted PAH were a bit delayed compared with the cohort of components but were also eluted following a size exclusion mechanism. It was, however, found that polyfunctional, polar compounds were eluted abnormally early, i.e. indicated

greater apparent MM. It is speculated that these components could account for a large peak at low retention volumes found for coal derivates. If the molecular weight of the peak was determined by the polystyrene calibration curve it would range up to 10^6 g/mol.

The results of Lafleur et al., 1989, were unusually good compared with previously applied SEC systems. They were followed up by a work of Johnson et al., 1997, and Herod et al., 1996, who demonstrated the advantages of using NMP as mobile phase compared to THF. By use of NMP the bulk of the analyzed coal-derived liquids were eluted prior to the permeation limit and a larger fraction of the sample was available for analysis. This work has inspired several works published within the last years (Lazaro et al., 1999a, Lazaro et al., 1999b, Begon et al., 2000, Herod et al., 2000a, and Herod et al., 2000b). All of these works have been published by a group of researchers from Department of Chemical Engineering and Chemical Technology, Imperial College, London.

A recent work (Lazaro et al., 1999a) has reexamined the retention mechanism by injecting pure pitch-related components. In contradiction with the predecessor (Lafleur et al., 1989) it was found that all relevant and available components were eluted within ±1ml (predominantly ±0.5 ml) of the polystyrene calibration curve. The results indicate that some of the problems with pure component calibration have been overcome. A serious drawback of the method is, however, that pure components are limited to the light end of the SEC chromatogram and thus leave the heaviest part uncovered by the calibration.

In analysis of coal-derived samples, a peak of material appears close to the exclusion limit of the column and prior to the retention of any available polystyrene standards. For the Mixed D column type (which will be used later in this work) the peak has smaller retention volume than the 200000 g/mol polystyrene standard. In all the works which have been reviewed it is found unlikely that pitch or coal-derived liquids actually contain large amounts of compounds with a molecular mass of this magnitude. There are two likely explanations of the composition of this peak: It could be caused by aggregates of smaller polar compounds. This theory was supported by the findings of Lafleur et al., 1989, that polar substitutes caused decreased retention. The other possibility is that the samples actually do contain large molecular compounds interlinked in a fashion causing them to be

excluded from the gel pores. These molecular species would then have molecular weights differing from the weight found from the polystyrene calibration. This standpoint is supported by the Imperial College Group, basing their arguments on re-injection of sample and heated-probe mass spectrometry (Lazaro et al., 1999a).

3.2.1.1 Fractionation

As stated in the earlier section it can be difficult to obtain a reliable calibration of a given SEC system by polystyrene standards and pure components. Since coal- and petroleum-derived materials consist of a very large amount of components it has been investigated whether the predominant separation has been weight-dependent. This can be investigated by fractionating a sample on a preparative SEC (meaning SEC column with sufficient throughput to obtain fraction yields to accommodate further analysis) and determining the average molecular weights of the fractions. This approach was used in the works of Boenigk et al., 1990, Bartle et al., 1984, and Brulé, 1980. The first author used pyridine as mobile phase while the two others used THF. All authors found that the relationship between molecular weight and elution volume was predominantly log-linear. Compared with polystyrene calibration the fractionated coal derivates (Bartle et al., 1984) and asphalts (Brulé, 1980) were eluted late. This is an important observation because it indicates that even systems which give rather poor results with pure component calibration are predominantly governed by a size exclusion mechanism, when the complex samples are viewed as a whole.

3.2.1.2 Direct Molecular Mass Detection

The ultimate goal in the development of SEC methods has always been to obtain a molecular weight distribution of the sample. The difficulties in making reliable calibration curves have led to approaches to obtaining a direct mass detection during the analysis. Some of the methods have been considered in connection with this work and a short overview will therefore be given.

The simplest approach is to use the polystyrene calibration curve and simply give the result in polystyrene equivalent molecular weight. The approach might not be very precise, but it gives an indication of the mass distribution and serves as a good illustration (molecular mass should then be given as *polystyrene equivalent*). Using the method also requires the assumption that the detector output is actually a direct function of sample concentration and this might not be the case (Brulé, 1980).

A method which has been investigated is the principle of universal calibration. The method is borrowed from the polymer science and is based on the Einstein viscosity law (Equation 3-1).

$$[\eta] = K\frac{V}{M}$$ Equation 3-1

[η]: Limiting viscosity index
V: Hydrodynamic volume
M: Molecular weight
K: Constant

Equation 3-1 predicts that [η]M is directly proportional to the hydrodynamic volume of the molecule and will therefore access the theoretic mechanism of separation in SEC. This approach has been seen to result in different types of polymers being represented by one calibration curve (Grubisic et al., 1967). Universal calibration has been applied to asphaltenes (Reerink et al., 1975, and Brulé, 1980) and coal derivatives (Bartle et al., 1984). All authors found that their calibration curves of the sample material differed from the calibration with polystyrenes. Even though the method might allow the same calibration to hold for various samples, it still fails to achieve a common calibration for polymers and the components of interest. It was considered to apply universal calibration but it was given up for two reasons. First, the limited viscosity [η] is typically measured by the change in pressure drop over a narrow tube. This could be difficult to obtain due to the similarity between the mobile phase and the sample components and it would add to an already high pressure drop in the system. Secondly, the advantages of using the method were not considered large enough to justify the effort.

Most of the principles concerning SEC have been borrowed from the polymer science. Lately, a new type of detectors based on multi-angle light scattering (MALS) has been marketed as a direct molecular weight detector in the range of 10^3-10^9 g/mol (Wyatt Technology Corporation, Santa Barbara, CA, USA). The method, however, requires an exact determination of the sample concentration. In the commercial detector (Dawn DSP) this is accessed from the signal by an RI detector. Unfortunately, this method cannot be used with the samples and the mobile phases of interest to this work.

3.2.2. Practical Use of SEC

Even though it has historically turned out to be difficult to obtain true molecular mass distributions, the most popular use of SEC has still been to obtain qualitative indications of molecular mass distributions. The real strength of SEC lies in the comparison between materials or fractionation.

If preparative SEC is applied the obtained fractions can be further analyzed, yielding information about the relationship between chemical composition and molecular mass. Boenigk et al., 1990, used SEC fractionation to obtain a molecular weight distribution of coal tar pitch. The pitch was fractionated by SEC and the yield and the molecular weight were determined for each fraction. The results showed that the majority of the pitch components had molecular masses below 400 g/mole, but the heaviest fraction turned out to have an average molecular mass of 2500 g/mole. Further analysis of the pitch fractions leads to the conclusion that the ratio of heteroatoms (N, S, O) is almost unaffected by molecular weight. This result is supported by Zander, 1991, and it indicates that the high molecular fractions of pitch are built up in a similar fashion to the lightweight components.

Lafleur et al., 1989, used SEC to pinpoint the similarities of the pyridine soluble part of coal from different geographic areas. Subsequently, one of the coal-derived materials was further fractionated by different solvents. Since liquids of similar origin often show very similar chromatograms further fractionation of the samples is usually applied in combination with SEC.

SEC has been used for pitch fractions, usually obtained by solubility, to achieve a fractionation according to functionality. Herod et al., 1995, used SEC of fractions obtained by planar chromatography to prove that the molecular weight was increasing with decreasing solubility. In later works SEC was used to determine whether a good separation had been obtained in an earlier process (Lazaro et al., 1999b).

3.2.3. Short Conclusion

Even though a true molecular mass distribution is not easily obtainable from SEC the main strength of the method is the comparison between similar samples. Choosing a strong solvent for the pitch as mobile phase can reduce the non-size effect. Good results have been obtained by use of the solvent N-methyl-2-pyrrolidinone at a column temperature of 80°C (Lazaro et al., 1999a, Johnson et al., 1997, and Lafleur et al., 1989).

3.3. Experimental Method

The SEC equipment is shown in Figure 3-3. The SEC system consisted of a Gynkotek, High Precision Pump, Model 300, delivering a mobile phase flow of 0.5 ml/min. Sample injection was performed by a Rheodyne 7725 valve fitted with a 20 μl sample loop. Separation was achieved by a 30 cm PL-Gel Mixed D column with a 5 μm guard column. Two different solvents were tested as mobile phase for the chromatographic system, tetrahydrofuran (THF) and N-methyl-2-pyrrolidinone (NMP). When THF was used as mobile phase the column was operating at ambient temperature with detection through an RI detector (differential refractive index detector). In the measurements with NMP as mobile phase the column was operating at 90°C. Detection took place by a DA (diode array) Detector, PE, Model 235C, with collection of UV absorption data at 300nm and 350nm. Samples were typically prepared as 2 g/l solutions, which were treated in an ultrasonic bath for at least thirty minutes and left to equilibration overnight. The samples were centrifuged before use to remove any undissolved material.

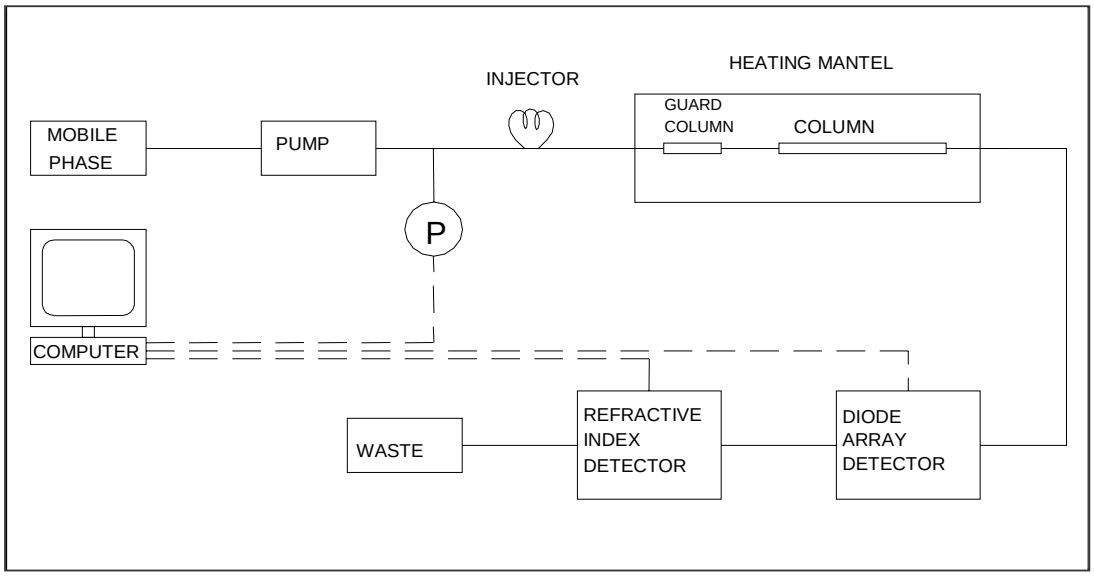


Figure 3-3: Chromatographic system.

3.3.1. Calibration

Initially, THF was used as a solvent. THF is a slightly better solvent for coal tar pitch than toluene (Guillén et al., 1991) and it may therefore be expected that all of the toluene soluble part of the pitch and part of the toluene insolubles could be analyzed by use of this solvent. Figure 3-4 is a calibration curve made by polystyrene standards. Some selected PAH components are included in the figure as individual plot points (naphthalene, phenanthrene, fluorene, fluoranthene, benz(a)anthracene, benzo(b)fluorene, coronene). It should be noted that the components cannot be represented by the polystyrene calibration curve and that the elution volumes are actually beyond the permeation limit of the system. One of the PAH was separated from the cohort of PAH plot points. This was coronene, which is a highly compact, pericondensed aromatic molecule.

Figure 3-5 shows a similar calibration with NMP as mobile phase and a column temperature of 90°C. The PAH compounds are now being eluted closer to the calibration line. It should also be noted that coronene is grouped with the other PAH. This might both be attributed to the better solvent power of NMP and to the fact that it is possible to run the column at a higher temperature due to the higher boiling point ($B_{p,}$(THF)=65°C,

$B_{p,}$(NMP)=202°C). Increased temperature reduces the interaction between solute and stationary phase.

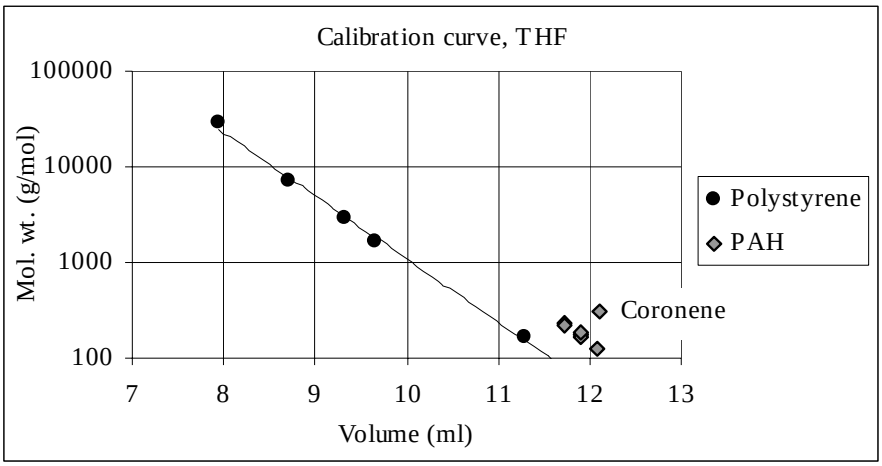


Figure 3-4: SEC calibration curve with THF as mobile phase.

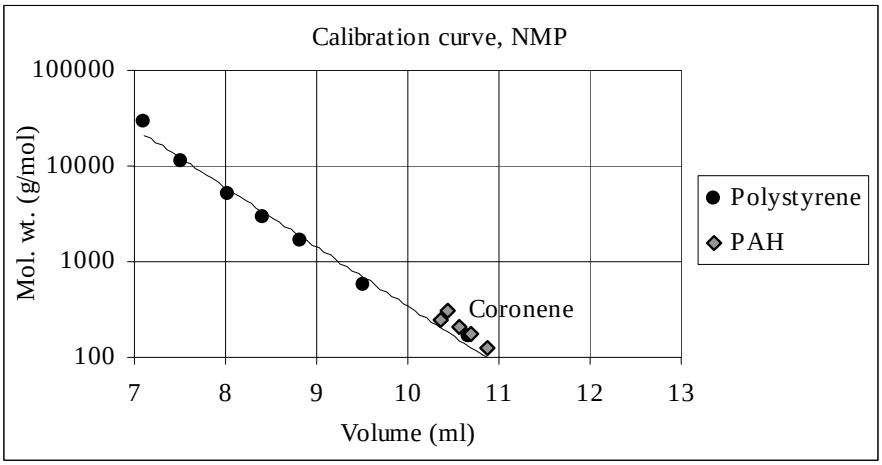


Figure 3-5: SEC calibration curve with NMP as mobile phase.

The position of the calibration line has shifted to lower elution volumes with the change in the mobile phase. The gel particles are in suspension in the mobile phase and swell when a better solvent is chosen. In other words, elution volumes can only be compared when the chromatographic system and solvent are the same. The calibration curves seem to indicate that a better size exclusion mechanism is obtained with NMP as mobile phase.

The SEC chromatograms of the pitch CTP A (Table 3-1), obtained by the two mobile phases, are shown in Figure 3-6. Two improvements are observed: 1) The elution of the pitch is moved within the size exclusion zone and 2) a new heavy material peak is appearing.

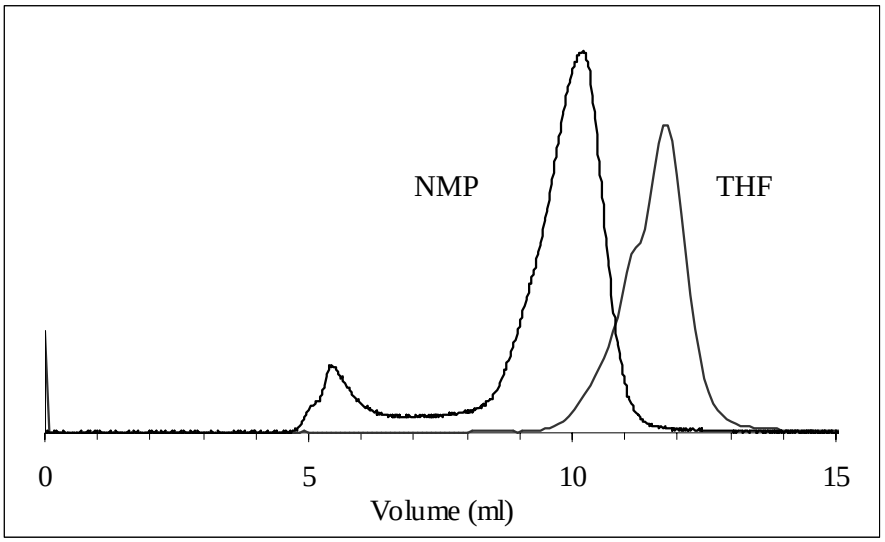


Figure 3-6: The sample CTP A analyzed by use of different mobile phases. Conditions: THF: ambient temperature, RI detector, NMP: t=90°C, DA detector.

When THF was used as mobile phase the peak maximum of CTP A occurred after the permeation limit. This indicates that the separation is not only due to size exclusion mechanisms but that some adsorption to the column packing is taking place. When NMP is used as mobile phase the entire pitch is eluted within the size exclusion zone.

The chromatogram obtained by NMP shows a new peak of early eluting material at the heavy end of the chromatogram. The greater solvent power of NMP means that a larger part of the pitch is soluble in the mobile phase and that this heavy material may therefore be analyzed by the new system. This is in accordance with the results of Johnson et al., 1997.

In the first chromatogram with THF an RI detector is used. This type of detector cannot be applied with NMP as mobile phase so for this system a DA detector is used. This means that the peak heights are not directly comparable.

Experiments showed that the detector output was linear with respect to sample concentration. This was found by running chromatograms of CTP A in various concentrations. The upper concentration level for pitch was 2.5 g/l. Higher concentrations caused the peak of late eluted components to be depressed due to the fact that the maximum detector output had been reached. At a concentration below 0.5 g/l the noise to peak ratio was unacceptably high. Thus, as long as the peaks did not exceed the maximum peak height the detector output could be scaled with respect to concentration. The flow rate of the mobile phase had some influence on the separation in the first peak. As a compromise between separation and analysis velocity it was chosen to run all analyses at a flow rate of 0.5 ml/min.

3.4. SEC of Pitch Fractions

CTP A was a commercially available coal tar pitch and it was used as received at Koppers Denmark (the properties are given in Table 3-1). This pitch was fractionated into solvent fractions by extracting ten grams of pitch by solvent followed by suction filtration to obtain the solution. This procedure was repeated until the washing liquid was colorless. The insoluble fraction was then washed with a stronger solvent. The soluble fraction was reduced in a rotation evaporator and dried in a vacuum oven. The pitch CTP A was fractionated by heptane, toluene, THF and NMP. The yields are given in Table 3-1. Fractions which had either been dissolved in NMP or washed with it could not be completely dried in the vacuum oven, so the yields do not add up to 100%. The fractions were given a code, which is also displayed in the table. Vapor pressure osmometry was used to determine molecular weights of the fractions by measuring four concentrations in pyridine at 60°C and extrapolating the readings to infinite dilution.

The heptane soluble part of the pitch (F-hep) has an average molecular weight of 265 g/mol. This is comparable to the weight of the pure PAH, which was analyzed earlier

(Figure 3-5). The SEC chromatogram of this fraction (Figure 3-7) consists of one sharp peak in the same range right before the permeation limit. The largest fraction of the pitch is the toluene soluble, heptane insoluble fraction (F-tol) with an average molecular weight of 413 g/mol. This material is apparently responsible for the light material peak of the pitch. There is an indication of a peak at the heavy end of the chromatogram.

	Unit	
SP (ASTM D-3104)	°C	115.5
QI (ISO 6791)	%(w/w)	7.4
TI (ISO 6376)	%(w/w)	26.8
CV (ISO 6998)	%(w/w)	59.1
Ash (ISO 8006)	%(w/w)	0.21
Density (DIN 51907)	g/ml	1.312
Mesophase (ASTM 4616)	%(v/v)	0.2

Solvent fractionation of pitch

Fraction	Code	Unit	Yield	Mol. wt.[b]
HS	F-hep	%(w/w)	7.5	265 g/mol
HI, TS	F-tol	%(w/w)	68.8	413 g/mol
TS, THFS	F-thf	%(w/w)	10.8	1044 g/mol
THFI, NMPS	F-nmp	%(w/w)	(10.0)[a]	-
NMPI	F-res	%(w/w)	(18.9)[a]	-

[a] Might still contain NMP [b] Measured by VPO

Table 3-1: Properties of the coal tar pitch (CTP A).

The THF soluble, toluene insoluble fraction (F-thf) has an average molecular weight of 1044 g/mol and the fraction is divided into two equal size peaks. The THF insoluble, NMP soluble material is eluted mainly in the first peak close to the exclusion limit. The material is eluted prior to the polystyrene sample with a molecular weight of 28500 g/mol so this range is not covered by the calibration curve. This example underlines that the calibration curve cannot be used directly for the heavy end of coal tar pitch. Unfortunately, it was not

possible to determine the molecular weight of the F-nmp fraction because it contained some NMP and was not completely soluble in pyridine.

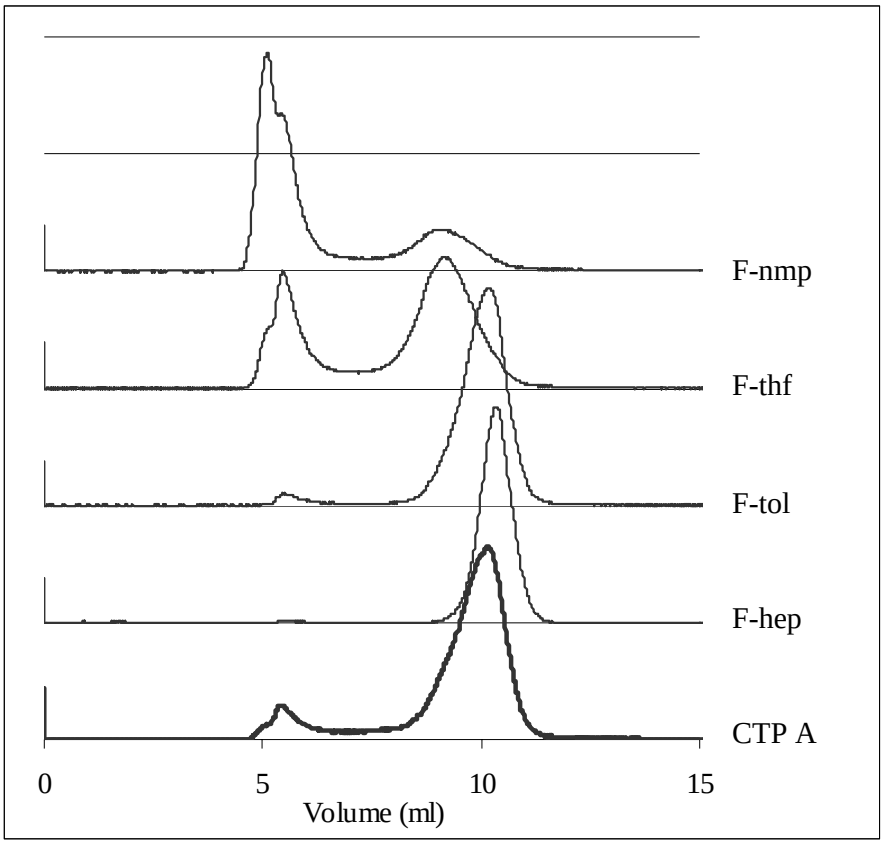


Figure 3-7: Size exclusion chromatograms of solvent fractions.

Experiments had shown that it was possible to scale the detector output by concentration. Following this line of thought, it was attempted to recompose the full pitch chromatogram from the chromatograms of the fractions by multiplying by the yield and adding the fractions. Figure 3-8 shows the recomposed chromatogram and the chromatogram obtained by direct analysis of CTP A. The recomposed chromatogram is similar to the direct analysis of the pitch. The late eluted material gives a slightly lower peak height in the recomposed chromatogram and the earliest eluted front shows a distinct peak. There are several plausible explanations for the addition of heavy material. Due to the fractionation a larger mass of the F-nmp fraction is analyzed. This up-concentration could lead to a larger fraction of barely soluble components actually being analyzed. If the early peak represents

associated molecules the larger concentration would further add to this process. There is also the possibility that the samples have been oxidized during the fractionation and especially the drying. This would lead to a larger concentration of heavier material. Unfortunately, the early peak is mainly based on the F-nmp fraction for which the yield could not be determined. If the addition of mass is pure NMP this should, however, become invisible in the SEC chromatogram and bring out the correct result. All in all, the chromatograms of the fractions give a good picture of the actual pitch composition.

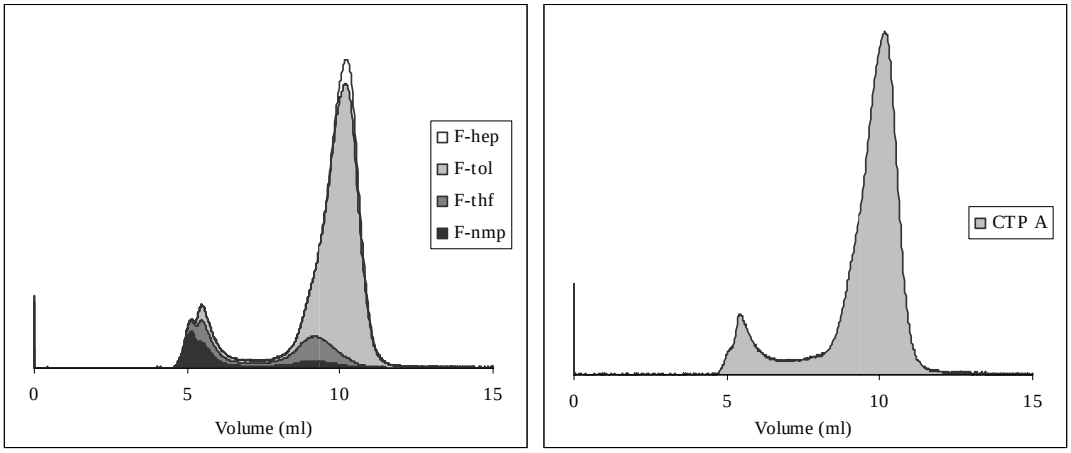


Figure 3-8: Illustration of the solvent fractions contribution to the pitch chromatogram. The left chromatogram is recomposed from the chromatograms of Figure 3-7 while the right is the chromatogram of the whole pitch.

Solvent fractions derived from the ISO 6791 and ISO 6376 standard methods were collected for SEC analysis (Figure 3-9). The toluene soluble fraction (TS) obtained by this method mainly consists of light material. All components of the pitch, which are eluted at the permeation limit, are contained in this fraction. There is, however, a clear indication of a peak representing heavy material. The toluene insoluble fraction was not completely soluble in NMP. The chromatogram of the TI fraction contains two peaks, one in the high molecular weight end of the chromatogram and one representing medium to low molecular weight material. The quinoline insoluble (QI) part of the pitch is almost completely insoluble in NMP. The part of the material which can be analyzed mainly consists of very heavy material with the possible inclusion of some light compounds.

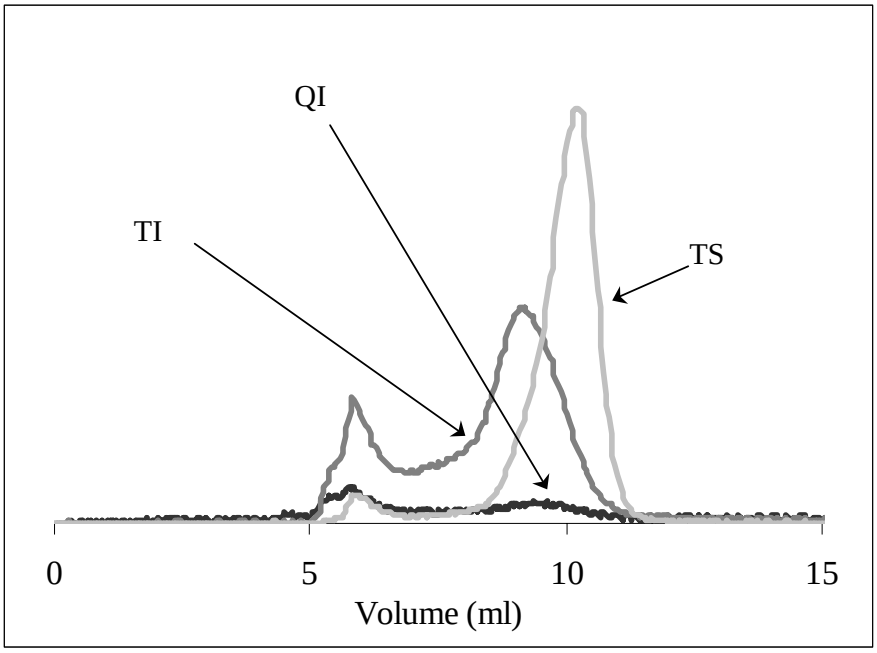


Figure 3-9: Size exclusion chromatogram of QI, TI and TS obtained from ISO 6791 and ISO 6376 methods.

3.5. SEC of Thermally Treated Pitches

The chromatographic method was used to analyze petroleum pitch samples which had received a thermal treatment for six hours at different temperatures prior to vacuum distillation (Section 2.3.1). The developments in the heaviest components were the main focus of interest. When the whole pitch was analyzed the small modifications in the pitch were hardly visible in the SEC chromatograms (Figure 3-10). The toluene soluble fraction was still the major part of the pitch and it was mainly eluted in the late light material peak, blurring the development of heavier species. It was therefore attempted only to analyze the TI fraction of the pitch.

Figure 3-11 shows chromatograms of the TI fraction and the entire pitch for the pitch K14 produced from a topped petroleum tar treated at 345°C for six hours. The chromatogram of the TI fraction has been multiplied by the yield of TI to allow direct comparison between the analyzed fractions of the pitch. By omitting analysis of the toluene soluble part of the pitch most of the late eluted peak is removed. The late part of the early eluted peak is

reduced with the removal of light material. The earliest front is a bit over-represented in the analysis of the TI fraction. This might be the same effect as observed at earlier fractionation (Figure 3-8). Providing that the development in the absolute, earliest eluted components is of main interest, the approach will magnify the tendencies.

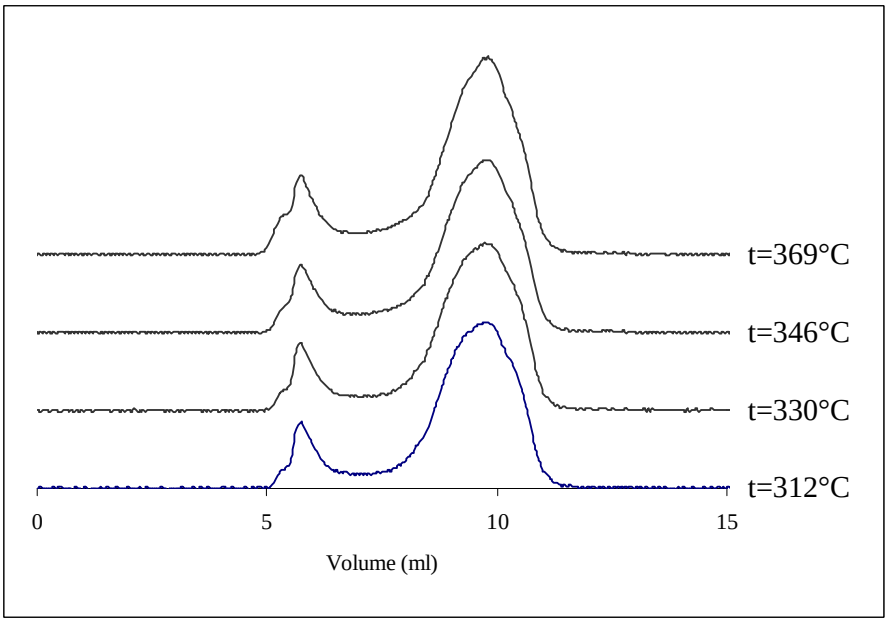


Figure 3-10: SEC chromatograms of thermally treated pitch. Treatment temperature of the topped tar as legend.

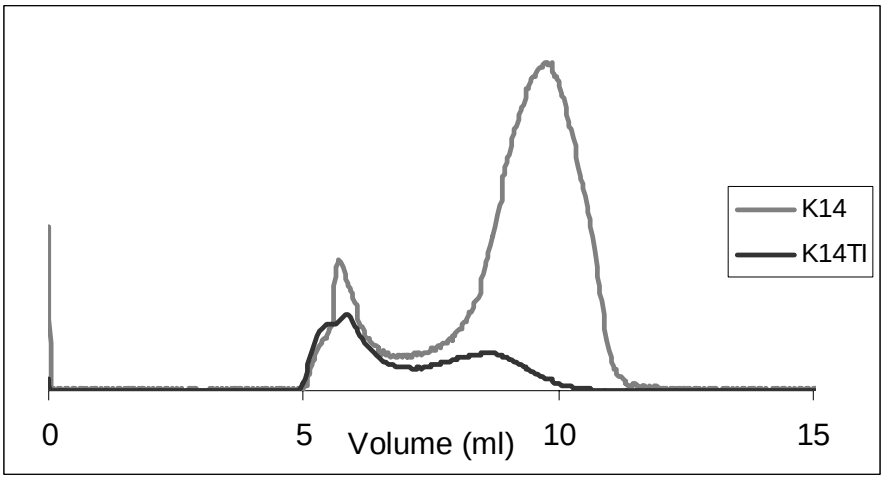


Figure 3-11: SEC of the entire pitch and of the TI fraction. Pitch produced from topped tar thermally treated for six hours at 345°C.

3.5.1. SEC of Petroleum Pitch

TI material was obtained by the ISO 6376 method. Once it had been established that this method was useful in the preparation of samples for SEC, TI material was collected routinely as part of the normal testing procedure minimizing the additional effort to obtain TI material. Figure 3-12 shows SEC chromatograms of five samples, which have received a thermal tar treatment at temperatures between 307°C and 415°C. In Figure 3-12 the sample concentration of TI material is kept constant at 2 g/l so that the chromatograms do not represent the development in the pitch but in the TI fraction.

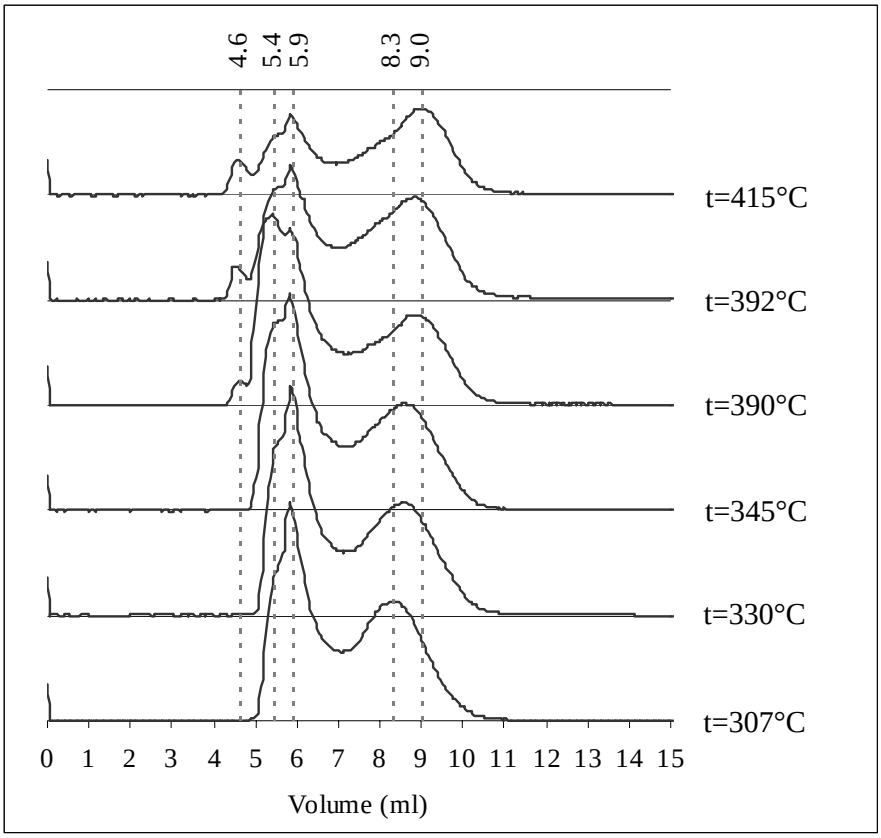


Figure 3-12: SEC chromatograms of TI fraction from tar-treated pitch samples.

As the temperature of the thermal tar treatment is increased, the peak at 5.4 ml is growing relative to the 5.9 ml peak. At the same time the last peak shifts to longer elution times. It has been observed that the elution volume of the maximum of the late peak is highly

dependent on TI. Solubility must be viewed as equilibrium between a solid phase and a liquid phase for every single compound in the pitch. Hence, it seems likely that the addition of heavier material influences and reduces the solubility of lighter components. This example emphasizes that the solubility fractionation is not absolute with respect to molecular species.

As the severity of the thermal treatment is increased a new peak of material eluted at 4.6 ml is formed. This peak has not been observed for untreated pitches or their fractions. The new peak is clearly caused by the thermal treatment and must represent components which do not normally occur in the pitch and tar. The peak is not present in the sample prepared from the topped tar thermally treated at 345°C while it is clearly distinct at 390°C.

The chromatograms of the pitches treated at 390°C and 392°C look very different. A comparison of the two chromatograms shows that the peak at 5.4 ml is strongly reduced and that material has been removed from the 5.9 ml peak as well. The main difference between the two samples is that the pitch which was produced by tar thermal treatment at 392°C contains visible mesophase (0.4%(v/v) by counting), while the other shows no visible mesophase. The formation of this liquid crystalline phase might account for the difference. In the chromatogram from the 415°C pitch further material seems to have disappeared from the middle peaks. Intermediate molecular weight components appear to be polymerizing to form very large molecules together with some “light ends”. This observation gives some new input about the fundamental process taking place in a part of the pitch which is not accessible by the most commonly used analysis tools.

The amount of TI material is increased as a result of the treatment (see Section 2.3.1). If the output level of the chromatograms is scaled to represent the whole pitch, it is noted that increasing severity of thermal treatment increases the content of material covering the entire molecular range (Figure 3-13). The pattern is broken when the treatment temperature is raised to 392°C and 415°C, where optically visible mesophase is found in the pitch. At these temperatures the amount of material in the new early peak and the light material peak continue to increase whereas the peaks at 5.4 and 5.9 ml are reduced.

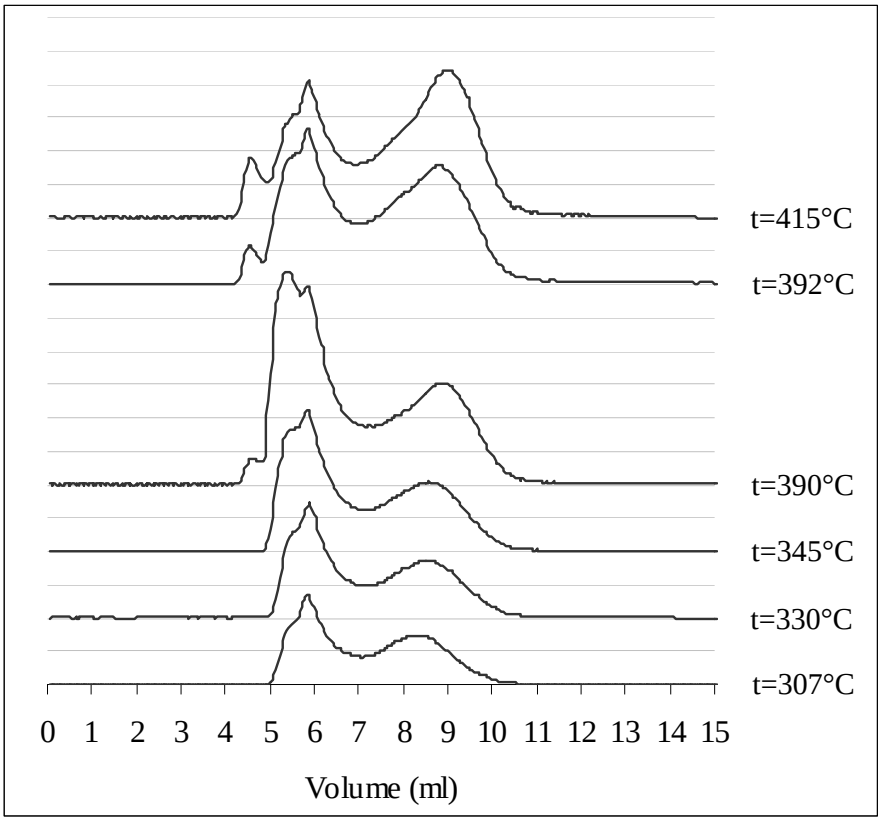


Figure 3-13: SEC chromatograms of TI fraction from tar-treated pitch samples. Detector output scaled by yield of TI from the pitch.

Figure 3-12 reveals that material appearing in the high molecular weight end of the chromatogram is being formed as a result of the thermal treatment. The nature of these peaks is the subject of an ongoing discussion. If the chromatographic system works ideally, the peaks should be caused by large molecular species. It has, however, been suggested that the peaks might also be caused by aggregates of smaller polar molecules (see Lazaro et al., 1999a, for further discussion). The fact that the early peaks are reduced in size by the formation of mesophase could be interpreted as formation of larger molecules which subsequently become mesophase.

In Figure 3-14 chromatograms of some of the TI fractions of the pitches manufactured by thermal tar treatments at 360°C for a range of time periods are shown. The chromatograms do not reveal any large development with increasing soak time. Lighter material seems to be added to the late peak with increasing treatment times. After the first two hours almost

no development is seen in the chromatograms. There is no formation of new, early peaks. The relationship between the peak heights is shown in the right graph as a function of the treatment time for the topped tar. This graph bears a similarity with the observed increase in TI content (see Figure 2-11).

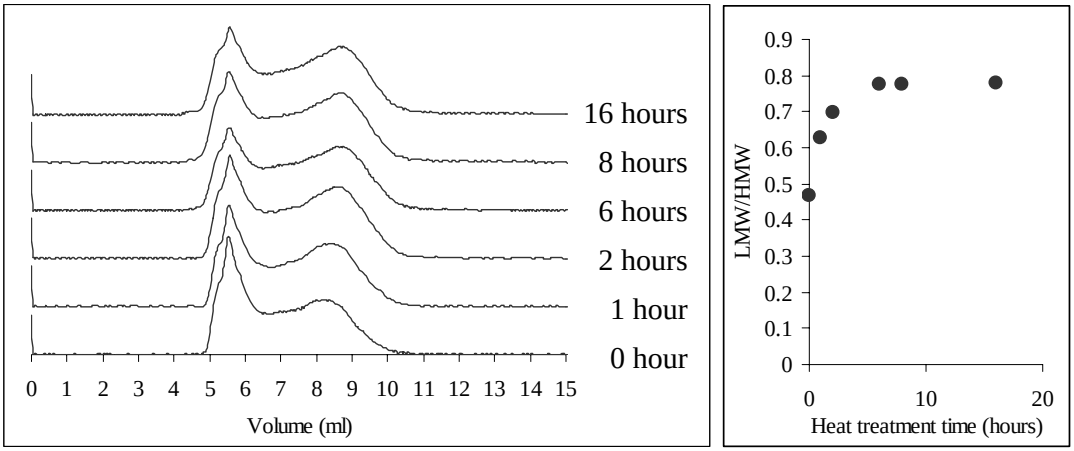


Figure 3-14: Left: SEC of pitch manufacture subject to thermal tar treatment of 360°C for different soak times (duration indicated). Right: Peak height of late peak divided by peak height of early peak as a function of treatment duration.

3.5.2. SEC of Blended Pitches

Pitches produced from blends of topped coal tar and petroleum tar thermally treated at different temperatures were analyzed by SEC. Following the procedure described earlier only the TI fraction was analyzed. The chromatograms are shown in Figures 3-15 to 3-19. Two of the analyses did not succeed and the chromatograms have been omitted from the figures. The chromatogram for the straight distilled coal tar pitch was eluted too early and the 80/20 blend thermally treated at 385°C showed an unlikely high amount of early eluted material. All the samples were analyzed over a short period of time just before the start of the anode study. At the time of analysis it had only been assured that chromatograms had been obtained for all samples, not that the results followed a certain tendency. It was decided to keep the integrity of the group by not rerunning samples almost a year later.

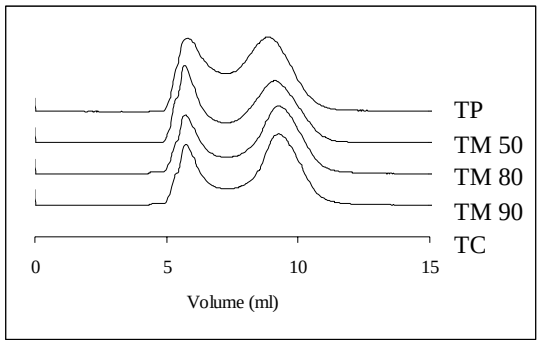


Figure 3-15: SEC of TI fractions from straight distilled pitch.

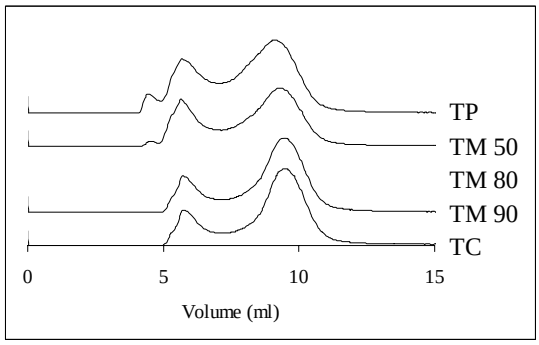


Figure 3-18: TI from pitch produced from topped tar thermally treated at 385°C.

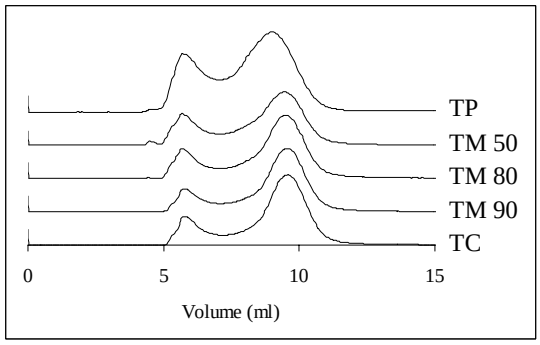


Figure 3-16: TI from pitch produced from topped tar thermally treated at 350°C.

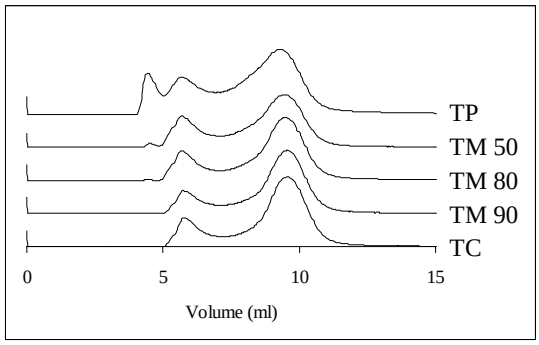


Figure 3-19: TI from pitch produced from topped tar thermally treated at 410°C.

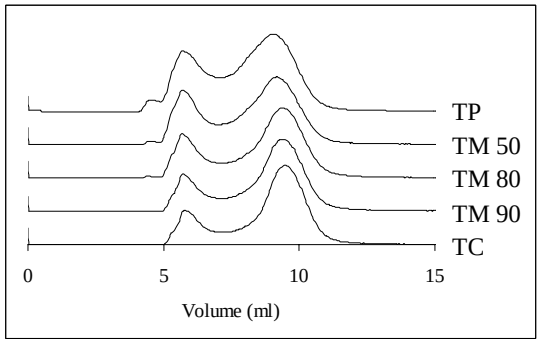


Figure 3-17: TI from pitch produced from topped tar thermally treated at 370°C.

Legend in Figure 3-15 to Figure 3-19:

TP: Topped petroleum tar

TM50: 50/50 blend of topped petroleum and coal tar

TM80: 20/80 blend of topped petroleum and coal tar

TM90: 10/90 blend of topped petroleum and coal tar

TC: Topped coal tar

The TI fraction of the coal tar pitch is almost unaffected by the thermal treatment. The amount of material actually eluted from the system is somewhat reduced as the

temperature of the thermal treatment is increased. There is no addition of new early eluted peaks.

The topped petroleum pitch proves to be just as sensitive to the thermal treatment of the precursor tar as the one described earlier (by comparison with Figure 3-12). The TI fraction in the pitch is strongly increased and it is observed that new components are formed which are eluted close to the exclusion limit of the column.

The analysis of pitches produced from thermally treated, combined material topped tars showed that these materials did not behave as it would be expected from pure pitches. In samples with a high content of petroleum-derived material or samples which have been subjected to a severer treatment an early peak is observed, but it is somewhat smaller than expected. The data presented in Section 2.5.3 strongly indicated that there was no interaction between coal-derived and petroleum-derived material. The SEC analysis surprisingly indicates a strong interaction between the materials.

Figures 3-20 to 3-25 show chromatograms of TI fractions from blended pitches derived from topped tar blends thermally treated at 370°C and 410°C. A calculated chromatogram combined of the pure petroleum pitch and the pure coal tar pitch is included to underline the divergence from ideality.

For the samples derived from topped tars thermally treated at 370°C there is a relatively good agreement between the calculated and the analytical results (Figures 3-20 to 3-22). Given the fact that the blend has both been thermally treated and distilled after the actual mixing this agreement is unexpectedly good. The SEC procedure has the advantage of only analyzing the TI fraction and thus removing most of the influence caused by the distillation. The agreement disappears when the samples are treated at higher temperatures. The early peak which is so distinct in the petroleum material is clearly being depressed by the coal-derived material. The main question is when the interaction between the two materials takes place.

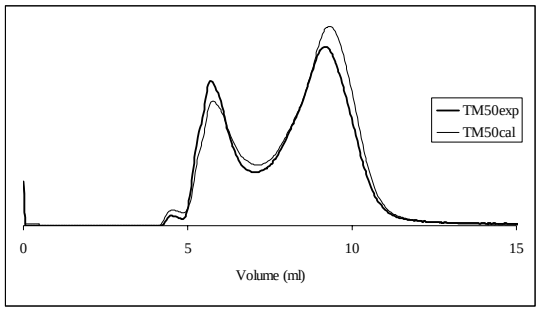


Figure 3-20: TI fraction from 50/50 blend thermally treated at 370°C. Experimental chromatogram and calculated from pure feedstocks.

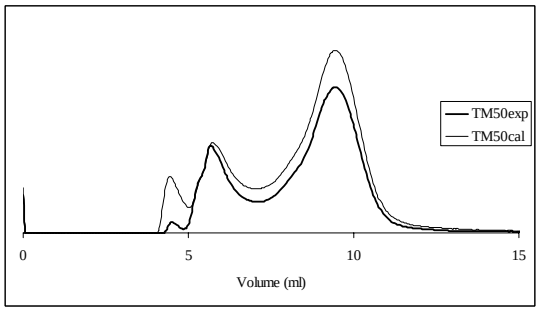


Figure 3-23: TI fraction from 50/50 blend thermally treated at 410°C. Experimental chromatogram and calculated from pure feedstocks.

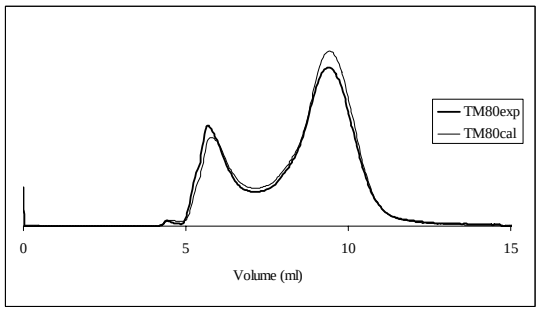


Figure 3-21: TI fraction from 80/20 blend thermally treated at 370°C. Experimental chromatogram and calculated from pure feedstocks.

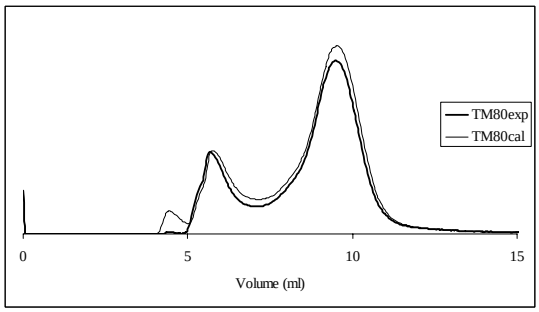


Figure 3-24: TI fraction from 80/20 blend thermally treated at 410°C. Experimental chromatogram and calculated from pure feedstocks.

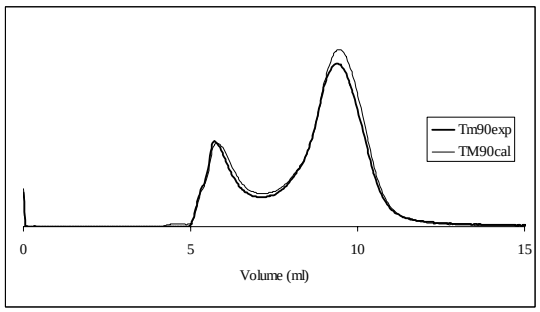


Figure 3-22: TI fraction from 90/10 blend thermally treated at 370°C. Experimental chromatogram and calculated from pure feedstocks.

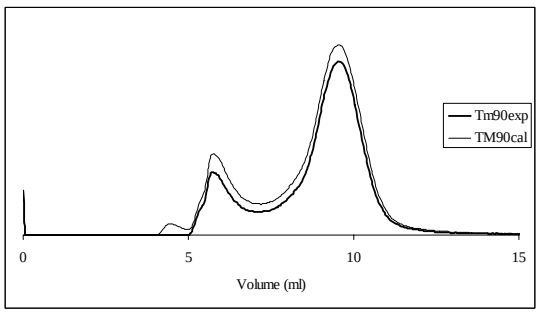


Figure 3-25: TI fraction from 90/10 blend thermally treated at 410°C. Experimental chromatogram and calculated from pure feedstocks.

One explanation could be that the presence of coal-derived material inhibits the polymerization which the petroleum-derived material would otherwise have experienced. This result is not supported by earlier analytical data presented in Chapter 2.

Another possibility is that the interaction has no relation to the thermal treatment but is a simple result of combining the two materials. The coal tar pitch contains natural QI particles which are similar to carbon black in structure. It is possible that the components are responsible for the formation of the early peak in the petroleum pitch but are simply absorbed to the surface of the QI particles.

It should be noted that the 50/50 blend shows traces of the early eluted peak for all treatment temperatures. This can, however, be explained by both theories, either as a larger concentration of reactive material or as a saturation of the QI particles.

Given the results which have been presented both in this chapter and in Chapter 2, it seems unlikely that an inhibition in the formation of large molecular species of petroleum origin would not have influenced either coking value or solvent fractions, which were both subject to investigation in Chapter 2. Thus, it seems more likely that some kind of absorption mechanism is interacting with the SEC analysis. This theory would also be in line with the reduction of peak size, which was observed in the study of pure petroleum pitch by the appearance of mesophase (Figure 3-12).

3.6. Fluorescence of SEC Fractions

Fluorescence spectrometry was used for further analysis of chromatographic fractions. The equipment was a fluorescence spectrophotometer (MFP-3, PE). It was operated in synchronous mode with a constant difference between the excitation and the emission wavelengths of 20 nm.

The theory of fluorescence is based on the energy levels of a molecule. The molecule absorbs light of a certain wavelength and energy by exciting an electron to a higher energy level. The molecule fast rearranges itself to the lowest energy level of the first excited state

without any energy radiation. The molecule can now return to the ground state by sending out energy as fluorescence. Due to the fast rearrangement to the lowest energy level of the first excited state, the fluorescence energy will leave the molecule as light with wavelengths characteristic of the molecule. Likewise the emission wavelength will always have lower energy and thus longer wavelengths than the excitation wavelength.

In classical UV fluorescence of one component the spectra are typically collected at either a fixed excitation or an emission wavelength. The complexity of the samples which are treated in this work as well as other studies of coal-derived or petroleum samples has led to the recording of synchronous spectra. When a synchronous spectrum is recorded the difference between the excitation and the emission wavelengths is kept constant ($\Delta\lambda=\lambda_{em}-\lambda_{ex}$=constant). It has been found that synchronous fluorescence spectra enhance characteristic peaks of the sample and give a clearer spectrum (Andersen, 1990). It is possible to interpret spectra with respect to molecular weights. As the molecular mass and the complexity of the molecular species increase, peaks typically shift to higher wavelengths and the intensity of the fluorescence is reduced (Andersen, 1990, and Lazaro et al., 1999a).

In order to obtain more information about the molecular structure, chromatographic fractions were collected and further analyzed by fluorescence spectrometry. Each fraction was a 1 ml cut of the chromatogram. The fractions were named fr1-fr15 (i.e. fr1: mobile phase eluted between 0 ml and 1 ml, see Figure 3-26). It was necessary to run four samples to obtain sufficient material. The fractions were transferred to the sample cuvette in the fluorescence spectrometer without further treatment.

Figure 3-27 displays the spectra for all the fractions from fr3 to fr12. The fractions collected between 9 ml and 12 ml gave the strongest fluorescence signals. This means that if a fluorescence detector had been used for the SEC, the chromatograms of the TI fractions had appeared as a single peak right at the permeation limit. The fraction showing the largest fluorescence is fr11, which was collected between 10 ml and 11 ml.

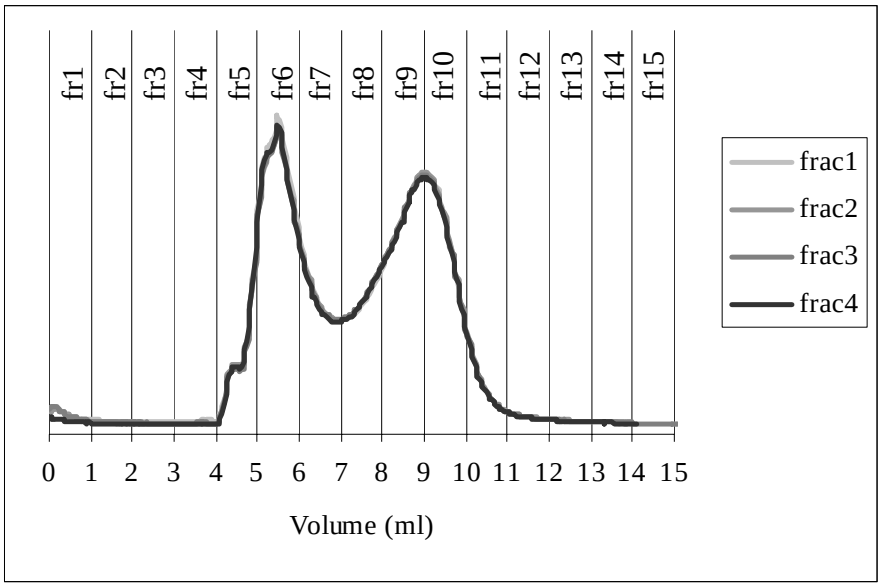


Figure 3-26: SEC fractionation of a petroleum pitch sample (tar thermally treated at 410°C).

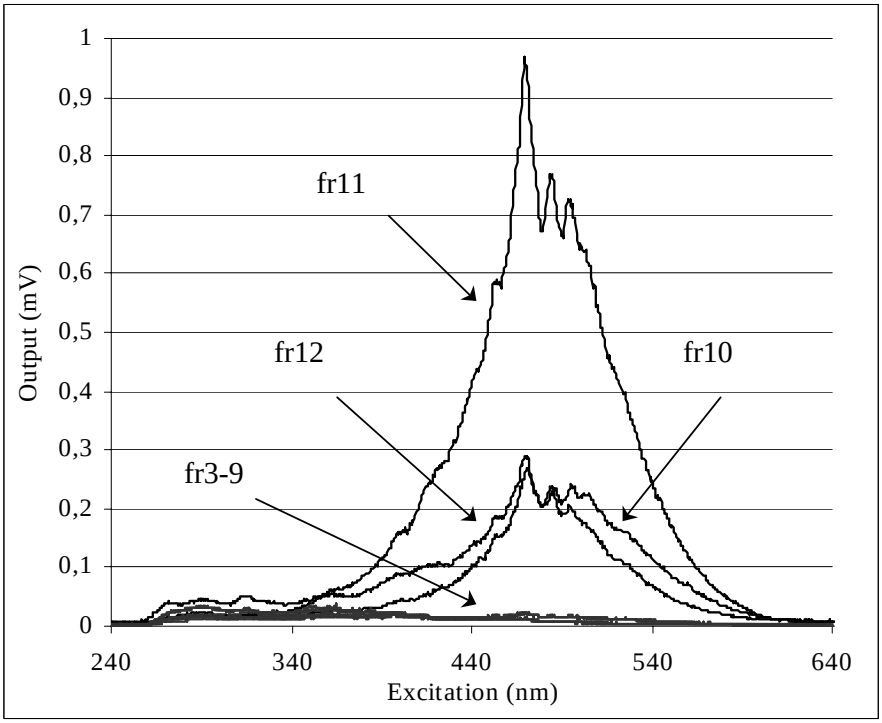


Figure 3-27: Fluorescence spectra of SEC fractions. Collected directly on the SEC fractions. Synchronous spectra with $\Delta\lambda$=20 nm, slit widths =5 nm, sensitivity= 30 %.

The fluorescence spectra of fr10 – fr12 show clear peaks at discrete emission wavelengths (Figure 3-27). If the intensity of the peaks is viewed in percentage of maximum intensity a shift towards higher wavelengths with lower elution volume is observed. This can be interpreted as an increase in molecular weight and is well in line with the SEC results.

In order to record spectra of the fractions which show low fluorescence the slit widths were increased to allow more light through the sample. Figure 3-28 shows four selected spectra for SEC fractions collected between 2 ml and 9 ml. In the wavelength range of 260-385 nm the intensity of the fluorescence from fr6-fr9 is lower than the fluorescence of pure NMP. At the higher wavelengths the intensity of the fluorescence is higher. The presence of very large molecules can manifest itself as absorption of fluorescence caused by internal energy quenching in the molecules (Mullins, 1998). Large molecular species are also known to have lower fluorescence intensity than smaller molecules. This supports the theory of large molecules in these fractions.

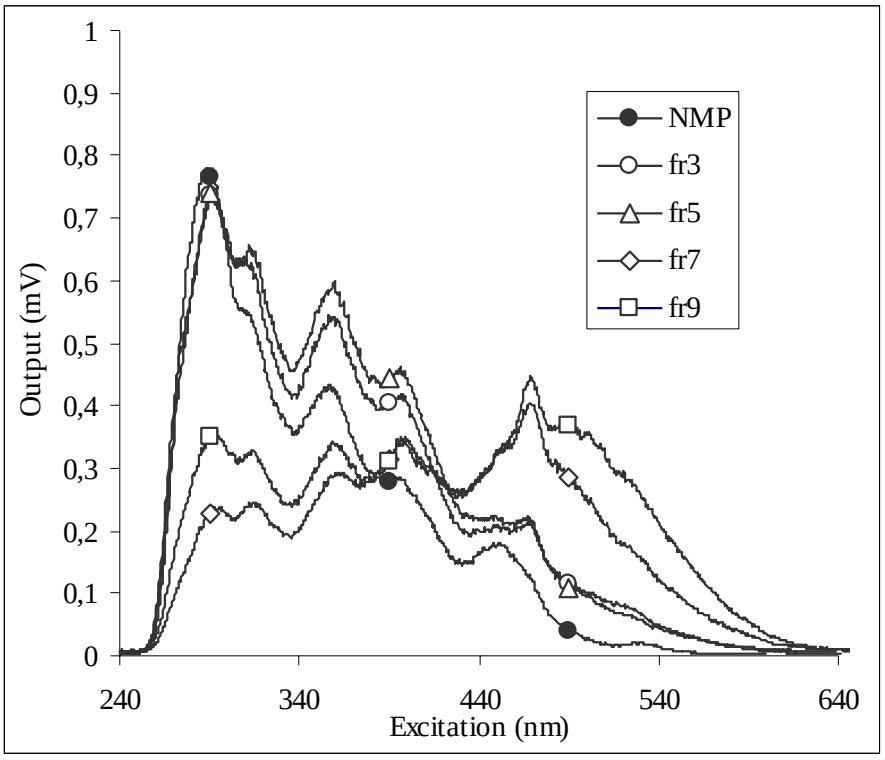


Figure 3-28: Fluorescence spectra of SEC fractions (see Figure 3-26). Collected directly on the SEC fractions. Synchronous spectra with $\Delta\lambda$=20 nm, slit widths=10 nm, sensitivity = 30 %.

The fraction fr5 is almost identical with the fraction fr3, which was collected prior to the exclusion limit, so the fluorescence spectrometry does unfortunately not give any indication of the nature of the fr5 fraction. Both of the spectra differ somewhat from the spectra of pure NMP. This could be attributed to absorbed material in the column slowly eluted over the entire range of the chromatogram.

Successful fractionation was reconfirmed by applying fluorescence spectrometry to SEC fractions. There is a clear indication of increasing molecular weight with decreasing elution volume for the SEC fractions. This enabled us to draw direct conclusions about the formation and disappearance of molecular weight classes based on SEC.

3.7. Conclusions on SEC

Size exclusion chromatography performed with a Mixed D column operated at temperatures between 80° and 90°C, NMP as mobile phase and a DA detector gives good analytical results. It has been indicated in several ways that separation is taking place following a size exclusion mechanism. PAH which were analyzed as pure components have been found to be eluted close to the polystyrene calibration curve. This is an improvement compared to the THF system where all of the PAH were eluted after the permeation limit. It is also found that pitch samples are fully eluted within the size exclusion zone and that the new mobile phase enables analysis of the entire quinoline soluble part of the pitch.

The size exclusion mechanism was confirmed both by analysis of pitch fractions and by analysis of chromatographic fractions by UV fluorescence spectrometry. A coal tar pitch was fractionated by solubility in heptane, toluene, THF and NMP. It was found that fractions with higher average molecular weight were eluted earlier than lighter molecular weight fractions. Further confirmation of the size exclusion separation was obtained by UV fluorescence spectrometry of SEC fractions. There was a clear indication of increasing molecular weight and complexity with decreasing elution volume.

In the analysis of pitches derived from thermally treated topped tars it was found that further information could be obtained by analyzing the toluene insoluble part instead of the entire pitch. This method underlines the processes which had been introduced by the thermal treatment.

It was found that early eluted species was formed as a result of thermal treatment. As the severity increased a new peak at 4.6 ml, which had not been observed in untreated pitch, started to appear. It was possible to connect the compounds eluted at 5.4 ml to the actual formation of mesophase. This information connects the visual appearance of mesophase to solubility of certain molecular weight classes.

SEC of pitch derived from topped tar which had been treated at 360°C for different time periods revealed no further development in the composition of the TI fraction after six hours. The majority of composition developments took place within the first two hours, thus confirming earlier described results.

SEC of blends indicated that there was an interaction between coal-derived and petroleum-derived in the pitch. Compared with earlier results this was unexpected. The coal-derived material was less sensitive to thermal treatment than the petroleum-derived material. Additionally, there was no formation of early peaks from this material. The blended material was acting more like coal tar material than petroleum tar. It could be speculated that the removal of the early eluted material could arise from either an inhibition during thermal treatment or by absorption of heavier molecules by the natural QI particles.

4. Microscopy in Pitch Analysis

One of the aims in this work has been to produce a good binder pitch. It might be useful to step back and consider what is actually required of such a material. At first the pitch is supposed to bind the grains of the coke filler together. At this stage the pitch has to act as glue not unlike the action of asphalt in the construction of road paving. In addition to the asphalt qualities, the binder pitch will, however, have to perform in a second process as well, the carbonization of the binder to produce solid carbon blocks. Coal tar pitch contains a solid fraction and this fraction has proven to have a huge influence on how the pitch will perform as an anode binder. This chapter reviews the nature and the significance of the solid fraction, followed by a characterization of some of the pitches which were produced during this work.

4.1. Nature and Significance of QI

Quinoline has proven to be a very powerful solvent for pitch (Guillén et al., 1991), and historically this solvent has been of large significance to the characterization of binder pitch. The background for this position is the unique solvent power of quinoline which enables it to dissolve the majority of the pitch components. The fraction which is not dissolved by quinoline is either actual solids or components brought close to a carbonized state by thermal treatment. The quinoline insoluble (QI) therefore plays a central role in the petrography of pitch even though the solvent is not used in the analysis.

It is useful to divide QI into two groups: Primary and secondary QI. Primary QI originates from coking of coal in the coke oven (see Section 1.2.1.3 for a description of the coke oven). The primary QI can be divided into coarser QI particles and carryover QI and a fraction of natural QI. Carryover QI originates from coal dust carried over from the coking chamber of the coke oven to the tar fraction. The most characteristic form of carryover QI is the cenosphere, which is formed in the coke oven from a small coal particle. The particle is transported into the headspace above the coal bed before it is coked. Here the high temperature causes the solid coal to enter the plastic stage, while gases from the coking reactions evolve within it. This rapid gas formation causes the particle to be blown up like

a balloon. The particle leaves the coking chamber with the tar and gas components and finally ends up in the tar with the other primary QI particles (Gray, 1989). In a good binder pitch the majority of the QI will, however, occur in the form which is called natural QI. This type is formed from tar components which have been carbonized in the headspace of the coke oven and the particles resemble carbon black. The presence of the natural QI particles is known to be beneficial to the binder phase.

Secondary QI is formed during processing of the tar to obtain pitch or during a later thermal treatment of the pitch. The process can be introduced either by high temperature treatment (typically at 430°C) or by excessive distillation of the pitch to a high softening point. As the first step of carbonization of pitch a liquid crystalline phase called mesophase is formed. The appearance of this phase is bound together with the formation of secondary QI. It has been shown that the two are not identical. Part of the mesophase components can be soluble in quinoline while part of the isotropic phase can be insoluble (Taylor et al., 1993). The formation of secondary QI can, however, be used to give a warning and a rough estimation of the amount of mesophase in a pitch.

The influence of the different types of QI on binder quality can be discussed. QI improves the coking value of the pitch. Most types do, however, have a negative influence on pitch viscosity and wetting ability. Natural QI is known to have a positive effect on the coke structure while primary QI originating from coal dust is unwanted due to its content of metal ions. Mesophase has generally been found to have a negative effect, due to the higher softening point, which prevents it from acting as binder. Some studies have found positive effects, because of the increased coking residue. In the present study, mesophase have been considered to have a negative influence and it has been attempted to avoid forming it in binder pitch. The natural QI particles are surface active to the mesophase interface. If a pitch contains both QI particles and mesophase, the natural QI particles will arrange themselves at the interface between the mesophase and the isotropic phase. This reduces the size of the mesophase spheres and gives smaller domains in the resulting pitch coke, again leading to higher strength. The types of structures which were observed in this study are listed in Table 4-1. Short descriptions as well as the significance to pitch usage are included.

Microscopic term	Nature and appearance	Significance during coking
Isotropic phase	Isotropic phase is the name for the non-optical active phase surrounding the mesophase. This phase is the continuous phase prior to and during early phases of mesophase formation.	The isotropic phase is the actual binder component in the pitch. This phase eventually turns into mesophase during carbonization.
Mesophase	Mesophase is a liquid crystal phase, which can be formed in pitch as the first step of crystallization. The mesophase appears as spheres which are visible in polarized light.	In a binder pitch the initiation of mesophase formation is unwanted because it influences the viscosity of the pitch negatively.
Natural QI	QI particles formed in the headspace of the coke oven. Normal QI is fully dispersed in the tar or pitch and can be seen as round particles of a size of less than one micron.	Natural QI are known to be surface active to the mesophase and to have a positive effect on the pitch coke structure.
Cenosphere	Cenospheres are formed from coal particles which are carried with the gas and the tar through the headspace of the coke oven. Due to the rapid heating, the volatiles of the coal particle will evaporate while the solids will enter a plastic state. This leaves the particle as a rounded shape with a hollow interior.	Cenospheres are unwanted because they contain the majority of the mineral impurities in the pitch.
Embryonic mesophase	Embryonic mesophase is defined as mesophase which is about to form. In a coal tar pitch, the QI particles tend to be caught on the surface of the mesophase particles. Prior to the actual formation of visual detectable spheres, the onset of a mesophase sphere can be detected as QI particle aggregates.	No reference has been found concerning the influence of embryonic mesophase on binder pitch performance.

Table 4-1: Overview of microscopic phases.

4.2. Detection of Mesophase

Some of the tar thermally treated pitches were investigated for mesophase (see Chapter 2 for further description of the pitch samples). The method used for determining mesophase in pitch was partly based on the standard method ASTM 4616-95.

4.2.1. Test Method

A piece of pitch ($1cm^3$) was molten in an epoxy resin. When the resin had been dried, it was ground to bring out a free surface from inside the pitch. The grinding took place on silicon carbide paper starting with grit number 80 and followed by grit numbers 220, 500, 800, 1200, 2400. The paper was placed on a rotating plate and the polishing lap was lubricated with water. The sample was held by hand and rotated 90° every time a new grit number of paper was used. Between the different grit numbers the surface was cleaned with water. The ground sample was polished on felt cloths with an alumina abrasive in water. The finishing polish was obtained by an alumina of 3 μm particle size followed by an alumina of 0.05 μm particle size. Ideally, the polish should remove all trace of grinding introduced scratches.

The sample was examined in a metallurgic microscope with dry lens. Magnification of x400 was used so that only spheres larger than 4 μm could be detected with certainty (according to ASTM D 4616-95). The amount of mesophase in the sample was determined by counting. A grid with 20x20 squares was placed in one of the oculars. The grid gave 441 points where the lines in the grid crossed. A random position on the pitch surface was chosen and all mesophase spheres situated under a grid point were counted. Ten positions on the pitch surface were counted and the concentration of mesophase was calculated by

$$Percent\ mesophase = \frac{Mesophase\ counts}{4410(total\ counts)} * 100\% \qquad \text{Equation 4-1}$$

4.2.2. Thermally Treated Samples

The majority of the pitches produced from thermally treated pitch did not contain any mesophase. For many of the samples the analysis mainly acted to ensure that they did not contain any mesophase.

In Figure 4-1 the mesophase content of petroleum pitches manufactured by a thermal treatment of six hours at different temperatures is shown as a function of QI (see Section 2.3.1). Only four of the pitches contained detectable amounts of mesophase. As a rule of thumb, a coal tar pitch must contain at least 1.3 %(w/w) secondary QI before mesophase becomes visually detectable (Malmros et al., 2000). This general rule has been found to apply for the pitches of petroleum origin and combined coal/petroleum origin (with one data point as the exception which proves the rule). In all the pitches examined, the amount of mesophase was lower that the amount of secondary QI.

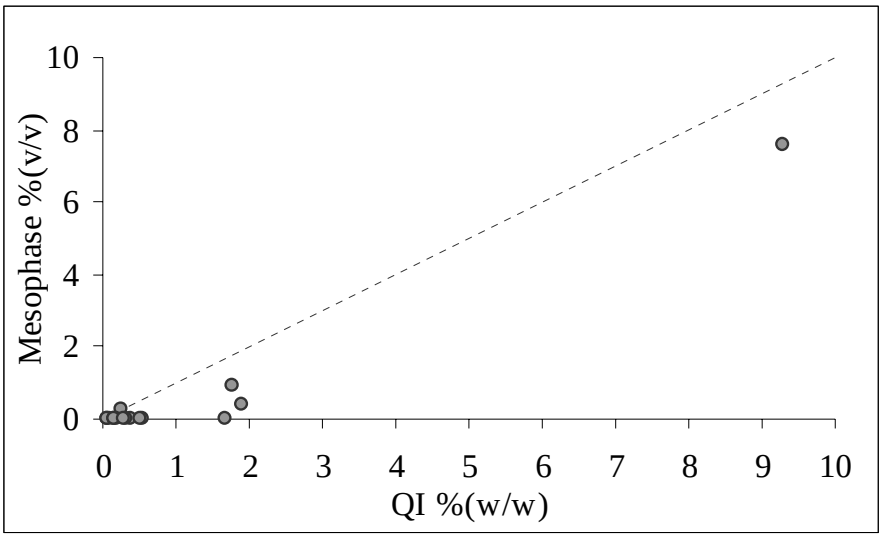


Figure 4-1: Mesophase as a function of QI. Pitch produced from thermally treated topped petroleum tar. The 1:1 line is shown on graph.

The petroleum pitch produced from a topped tar thermally treated at 415°C contained 7.6 %(v/v) mesophase by counting. This pitch sample was the only pitch which contained coalescent mesophase (Figure 4-2, Picture A). When the pitch was poured out of the distillation flask to a storage container it was observed that it contained lumps. One of

these lumps was molted and polished for microscope examination. Inside the lump a large area of coalescent mesophase was found (Figure 4-2, Picture B). The lumps were found in the bottom of the distillation flask but the appearance of the coalescence mesophase does not suggest that they were formed on the surface of the distillation flask during thermal treatment. It is more likely that they have moved to the bottom of the flask by gravitation. Since the lump was not taken into account in the analysis the actual mesophase content in the pitch could have been higher than reported. The experimental thermal treatment procedure which was used in this study was not suited for treatments yielding substantial amounts of mesophase in the resultant pitch.

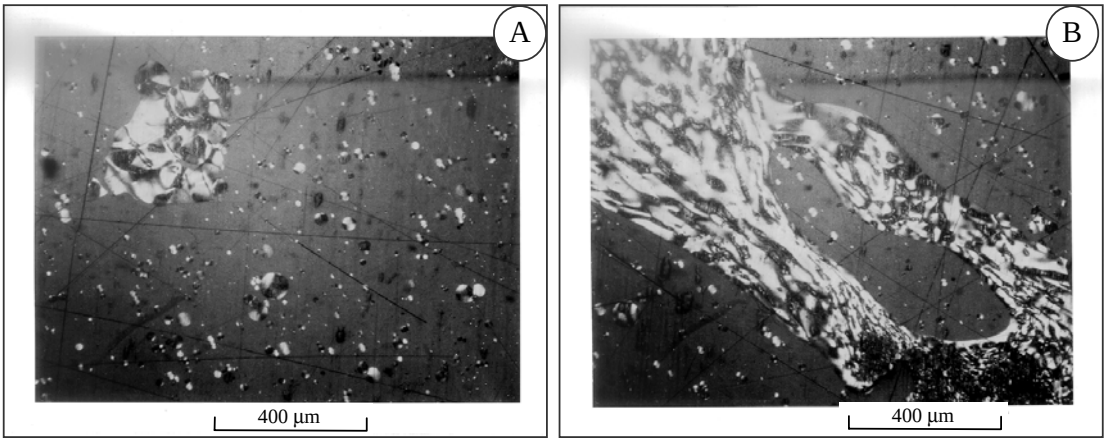


Figure 4-2: Pictures taken in the Koppers Denmark laboratory. Sample: Tar thermally treated at 415°C (K18), x100, polarized light. A: Typical pitch sample, B: Sample of lump in the pitch.

The pitches which were produced from the thermally treated blend of coal tar were examined for mesophase (Section 2.3.3). The pitches derived from topped tars treated at 350°C and 370°C showed no signs of mesophase. One of the pitches from the 385°C treatment showed a low concentration of mesophase while two of the pitches tar treated at 410°C contained no detectable amounts of mesophase. The analytical results are given in Table 4-2.

The mesophase analysis seems to predict that a temperature of at least 385°C is required to cause mesophase in the produced pitch. The amount of formed mesophase can, however, not be predicted on the basis of the results. The pitches produced by the 410°C treatment generally contain more mesophase than the pitches produced via lower temperatures, so

that treatment temperature seems to have a certain influence. On the basis of literature it was expected that the petroleum material would show higher mesophase content than the coal tar material due to the influence of primary QI. This expectation was confirmed by the 4.9 %(v/v) mesophase found in the petroleum-derived pitch, while no mesophase was found in the coal tar pitches. The blends, on the other hand, did not follow the expected tendency, actually the 50/50 blend contains no visible mesophase while the 90/10 blend contains 1.5 %(v/v). The appearance of mesophase is often connected with secondary QI. Figure 4-3 shows mesophase content and secondary QI as functions of the content of topped coal tar for the 410°C pitches. There seems to be no actual connection between the two analytical results.

Topped coal tar % (w/w)	Mesophase, t=385°C % (v/v)	Mesophase, t=410°C % (v/v)
0	0.00	4.92
50	0.00	0.00
80	0.00	0.50
90	0.14	1.50
100	0.00	0.00

Table 4-2: Mesophase content in the pitches produced from thermally treated tar.

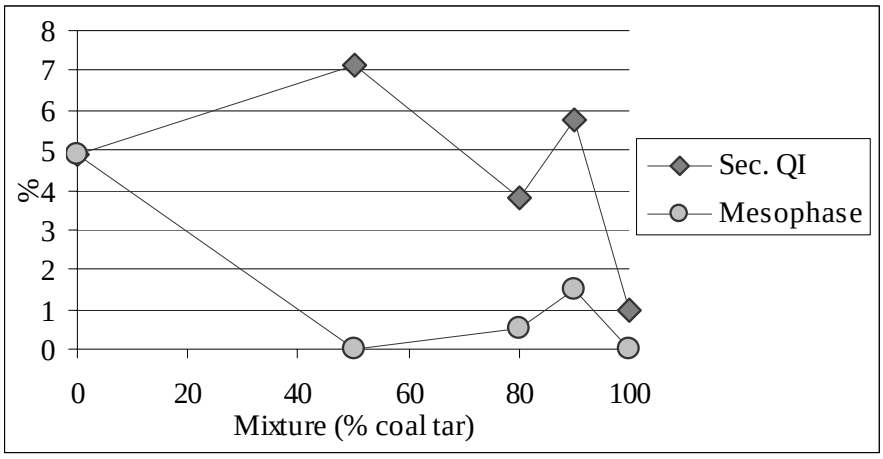


Figure 4-3: Mesophase content and secondary QI versus the percentage of coal-derived material in pitches produced from blended, topped tars which have been thermally treated at 410°C

4.3. Analysis of Pitch for the Anode Study

The four pitch samples, which had been manufactured for the anode study including a thermal treatment (see Chapter 6), were sent to Ralph Gray (RG) for petrographic analysis and he very kindly allowed the presence of the author during the analysis to share some of his experience. RG has a long experience in petrographic analysis of coal, anodes and coal tar pitch. Four samples were chosen for the petrographic analysis, a pure coal tar pitch (CTP_{T1}), a pure petroleum pitch sample (PP_{T1}) and two combined coal/petroleum samples (MIX_{T1} and MIX_{T2}). All the samples had received a six-hour tar thermal treatment at 385°C as part of the preparation. The method of combining the two blended materials differed in that the sample MIX_{T1} was a 80/20 blend of the pitches CTP_{T1} and PP_{T1}, while MIX_{T2} was obtained from a thermally treated 80/20 blend of the precursor topped tars (Section 6.2.1). RG's petrographic equipment RG allowed detection of very small amounts of mesophase so one objective of the analysis was to determine whether some of the samples had formed mesophase. Another objective was to study how well the two blended materials had been combined and whether there was any visible unhomogenized areas in the blend.

The pitches were prepared for microscopy according to the ASTM D 4616-95 standard by a commercial laboratory (Coal Petrographic Associates, Pennsylvania). The preparation method deviated from the Koppers Europe method in two important ways. First, the slide was made from a finely ground pitch which was melted and molten in epoxy resin within a 25mm Bakelite ring. All four samples were fitted in a special holder and ground simultaneously. During the grinding and polishing the holder rotated so that there was no preferred polishing direction. The grinding took place on grit number 240 followed by grit number 400 and 600 SiC-papers. The slide was polished on silk-cloth with 0.3 and 0.05µm alumina as polishing agent.

The first visual impressions of the four pitches are shown in Figures 4-4 to 4-7. A comparison of the four pitch types shows first of all that the petroleum pitch differs much from the other three samples. The coal-derived material contains small QI particles and in the picture of the coal tar pitch (Figure 4-4) a large cenosphere has been captured. The

blended pitches look very similar to the coal tar pitch. There are no distinguished, recognizable features in the petroleum pitch (Figure 4-5). The surface does, however, show traces of some indistinguishable irregular patches. The nature of these patches will be discussed in Section 4.4.

Figures 4-8 to 4-11 show microscope pictures of the four pitches taken under a magnification of x1000 while pictures taken under a magnification of x2000 are shown in Figures 4-12 to 4-15. When the figures are studied in the following section it should be noted that some of the figures have a greenish color while others have a reddish/brown appearance. The green color is an artifact caused by filters applied in the photo laboratory during the print of one of the films. The film was treated as normal holiday pictures and therefore a green filter to magnify outdoor colors was used.

The coal tar pitch and the blends contained natural QI. It was observed that the particles had started to form aggregates. A good example of the aggregation can be seen in Figure 4-12 right of the easily recognizable contour of the cenosphere. According to RG the QI particles will form aggregates prior to mesophase formation. As the mesophase formation propagates it is possible to detect small areas of mesophase within the aggregates. These formations can be defined as embryonic mesophase. The fact that QI particles arrange themselves on the surface of mesophase spheres was discovered almost immediately after the discovery of mesophase itself and is mentioned already in the article by Brooks and Taylor, which is recognized as the first central article concerning mesophase in pitch (Brooks et al., 1965). It appears intuitively reasonable that the association of the QI particles with the mesophase could cause agglomeration of the natural QI particles as the first visible sign of mesophase formation.

Using a magnification of x1000 (Figure 4-9) shows that the petroleum pitch contain small mesophase spheres and an irregular patch (IP). Within the IPs, structures which appear similar to QI particles are found (Section 4.4). In Figure 4-13 an area with several of the mesophase spheres is shown. Almost all of the spheres are less than 4 μm and would thus have been below or close to the detection limit of the Koppers Denmark microscope.

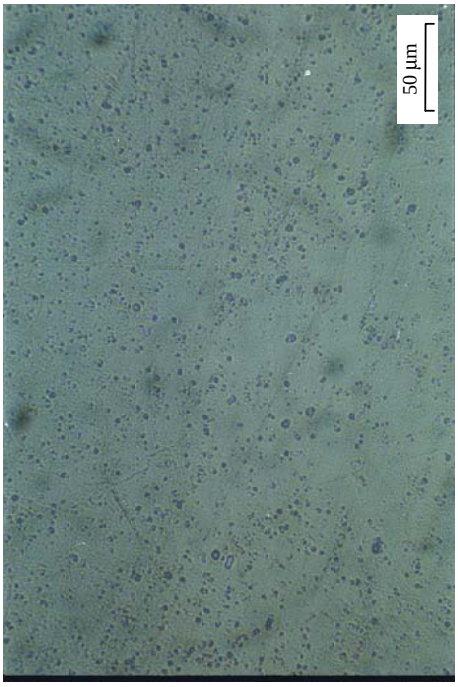


Figure 4-6: Pitch produced from blended tar. x325 (oil).

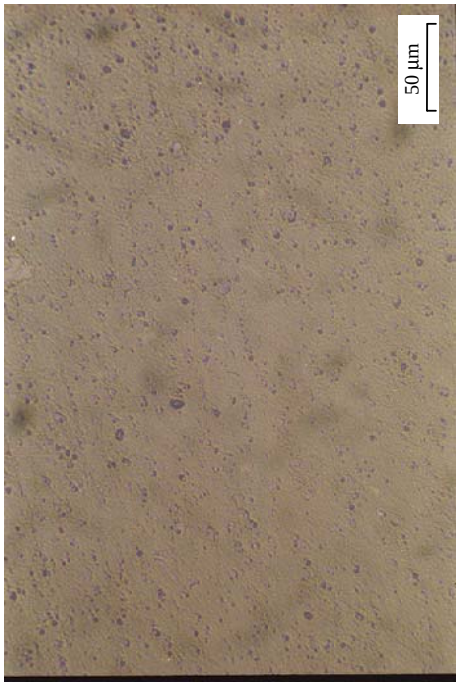


Figure 4-7: Pitch blend of CTP and PP. x325 (oil).

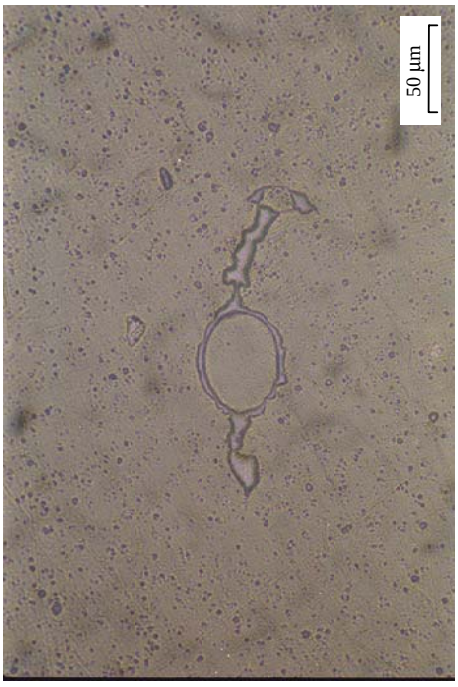


Figure 4-4: Coal tar pitch for anode study. x325 (oil).

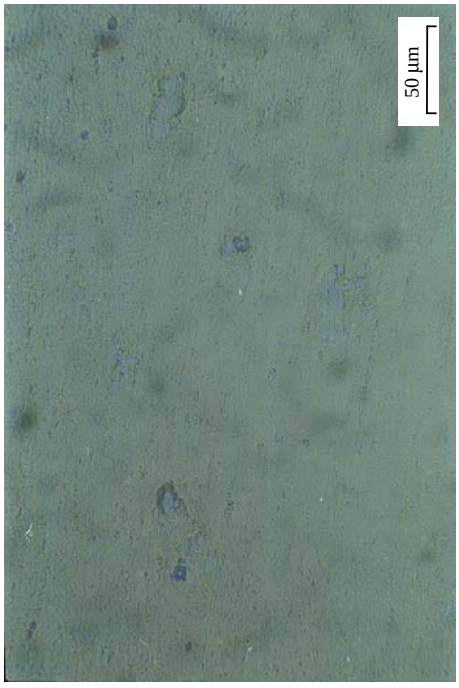


Figure 4-5: Petroleum pitch for anode study. x325 (oil).

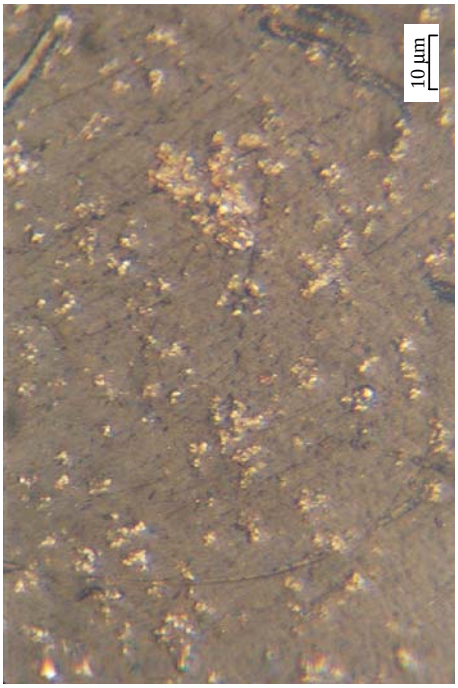


Figure 4-10: Pitch produced from blended tar. x1000 (oil).

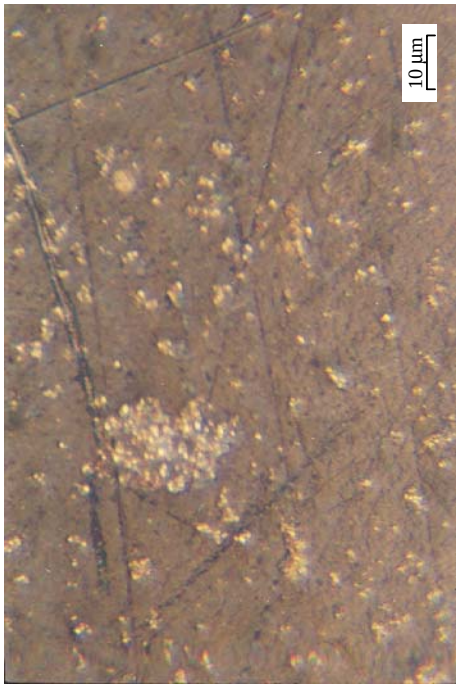


Figure 4-11: Pitch blend of CTP and PP. x1000 (oil).

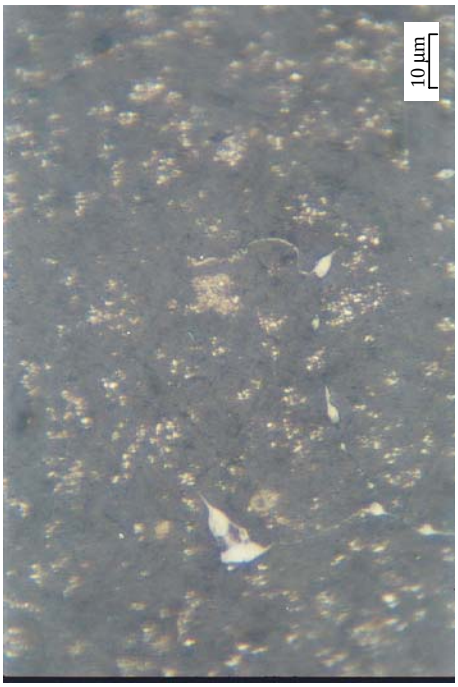


Figure 4-8: Coal tar pitch for the anode study. x1000 (oil).

Figure 4-9: Petroleum pitch for the anode study. x1000 (oil).

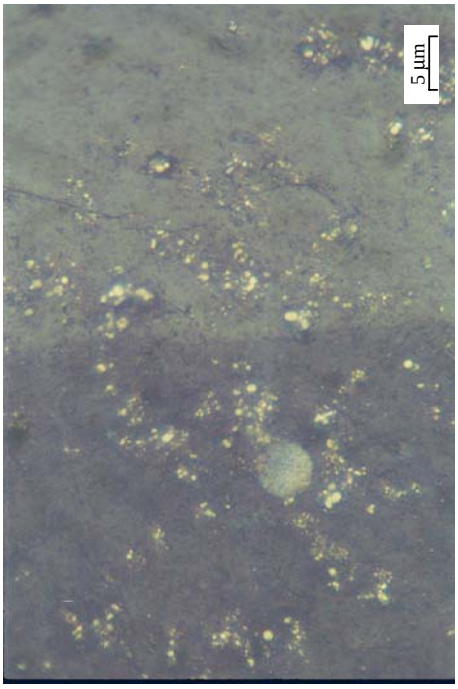


Figure 4-14: Pitch produced from blended tar. x2000 (oil).

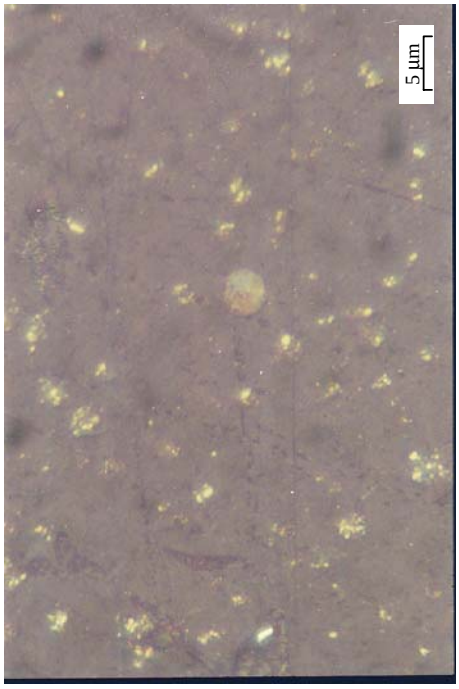


Figure 4-15: Pitch blend of CTP and PP. x2000 (oil).

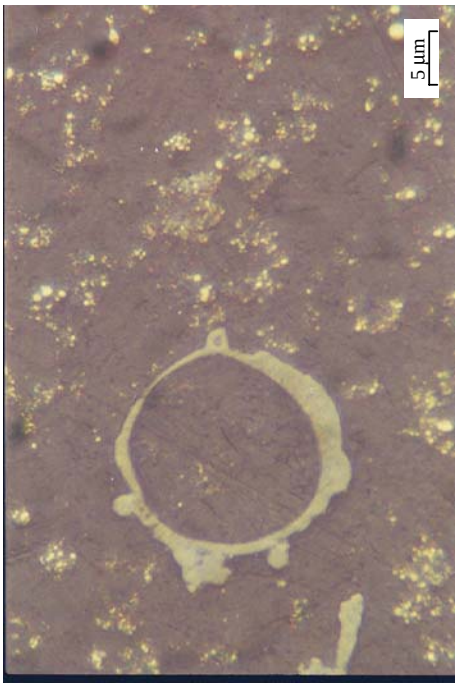


Figure 4-12: Coal tar pitch for anode study. x2000 (oil).

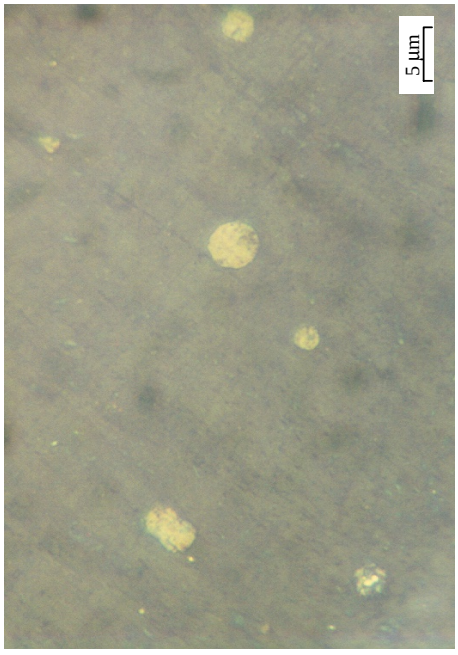


Figure 4-13: Petroleum pitch for anode study. x2000 (oil).

The two blended pitches are both very similar to the coal tar pitch. The petroleum material seems to be well integrated with the coal tar material yielding an even distribution of the QI. Table 4-3 gives the results of the petrographic analysis performed by the Ralph Gray Services. In the blends the total amount of primary QI is reduced in proportion to the amount of added petroleum material, which indicates that a homogeneous blend of the two materials has been obtained as well as a representative sample. According to the direct analysis or the QI of petroleum pitch and tar, this material should not contain any primary QI. In Table 4-3 the petroleum pitch is listed with a content of natural QI of 0.6 % due to the material found within the IP (Figure 4-9).

	CTP_{T1}	PP_{T1}	MIX_{T1}	MIX_{T2}
Continuous binder phase	88.7	98.3	90.6	91.1
Embryonic binder phase	3.9	-	3.2	2.7
Total binder phase	92.6	98.3	93.8	93.8
Normal QI	1.2	0.6	1.0	0.9
Coarse QI	0.4	-	0.1	0.2
QI in embryonic	4.9	-	4.3	4.3
Total QI	6.5	0.6	5.4	5.4
Mesophase < 2 microns	0.5	0.3	0.3	0.6
Mesophase 2-4 microns	0.2	0.4	0.3	0.1
Mesophase 4-10 microns	0.2	0.3	-	-
Mesophase +10 microns	-	0.1	0.2	0.1
Total mesophase	0.9	1.1	0.8	0.8
Grand total	100.0	100.0	100.0	100.0

Table 4-3: Petrographic analysis of anode pitch. The petrography was performed by Ralph Gray services.

The coarse QI particle in the coal tar pitch was subjected to a further analysis to obtain a more detailed picture of the exact origin of the particles. The particle types and frequency are listed in Table 4-4. Part of the coarse particles could be recognized as cenospheres or cenosphere fragments. A large fraction of the coarse particles is found to be angular isotropic and anisotropic forms, which are listed as “undetermined”. It was not possible to

determine the origin of these particles but they were all carbon-based. Pyrolytic carbon, pitch coke and coke are formed in pipes and on heater surfaces during the handling of the tar and pitch. The pyrolytic carbon is formed on the upper walls, the tunnel head and the standpipes of the coke oven while the pitch coke is formed during distillation or heat treatment in the production of pitch. Mineral matter originates from fine coke particles which are digested in the tar, resulting in a residue rich in mineral matter (ASTM D 4616-95).

Size (μm)	Cenosphere	Un-determined	Pyrolytic carbon	Pitch coke	Coke	Mineral
3-10	20	25	3	-	-	4
10-20	8	15	1	2	1	-
20-40	6	6	-	2	-	-
40-60	1	3	-	-	1	-
60-80	1	1	-	-	-	-
80-100	1	-	-	-	-	-
+100	-	-	-	-	-	-

Table 4-4: Frequency distribution by size of coarse particles in CTP_{T1}.

The content of coarse particles is not very large and the majority of the particles are of a size below 60 μm. The majority of these particles are fragments of cenospheres or angular carbon shapes whose origin could not be determined. The nature of the coarse particles was only determined for the coal tar pitch because there were no coarse particles in the petroleum pitch and all coarse particles in the blends seemed to originate from the coal tar.

4.3.1. Conclusion Based on the Petrography of Anode Pitch

The petrography of the four different pitches revealed that they had been thermally treated. Some of them contained visible mesophase formation. This is particularly visible in the petroleum pitch. In the pitches which contain coal derived material, aggregation of the natural QI particles can be seen indicating embryonic mesophase formation. If the ASTM 4616-95 standard is used most of these formations are below the detection limit due to less powerful magnification.

The coal-derived and the petroleum-derived materials of the blended pitches have been well integrated. There is no visible difference whether the materials have been combined prior to the thermal treatment as topped tars or as fully prepared pitches. Both pitches are similar to the coal tar pitch in appearance.

The petroleum material did not contain primary QI material when analyzed directly (Chapter 2). In the petrographic analysis it is listed as containing 0.6 % normal QI. This amount probably derives from material in the irregular patches being counted as natural QI (see Figure 4-9). The mesophase spheres in this pitch are easier to detect compared with the other pitches. When all the material is added the amount is, however, more or less the same in all the four samples.

4.4. Identification of Irregular Patches Found in Petroleum Pitch

In the petroleum pitch PP_{T1} a strange irregular patch (IP) was observed (Figure 4-9). Similar patches had often been observed during the study of petroleum-derived pitches in the Koppers Denmark laboratory. According to Ralph Gray, this sort of patches is only found in petroleum material. It was speculated that some sort of pyrolytic carbon from the manufacture of the ethylene cracker bottom could be the cause of the patch and it was attempted to discover the nature of the appearance.

4.4.1. Thin Section Microscopy

It was attempted to make a quick test to see if there were any strange features in the petroleum sample. A small piece (<1mm ø) of PP_{T1} was placed on a microscope glass slide and softened with a drop of toluene. The mixture was pressed to a thin layer with a cover glass. When the slide was studied in transmitted light, a black residue of very fine particles was observed in the original position of the pitch. The toluene soluble part had floated to the rim of the cover glass and appeared as a clear red ring. If a slide was prepared by melting the pitch instead of softening it with solvent, the black dots were evenly dispersed in the pitch. The observations were interpreted in the way that the petroleum pitch had to contain a form of small carbon particles, which were not known from coal tar. Since

petroleum tar is a by-product of ethylene and the precise operation conditions of this particular product are not known in detail, it seems likely that it might contain this type of material. This sort of particle could result in the IP.

A problem in the experiments was that features observed in reflecting light in a polished surface could not be connected directly to the features observed in thin sections. The isotropic phase is the wetting phase, meaning that no mesophase or coarse QI will arrange itself at the interface to a glass or air. The surface of a thin slide was therefore found to be featureless. This problem could be solved if a slide with a polished surface could be obtained.

Polished thin sections are standard preparation in the study of minerals and rocks. A pitch sample was sent to a commercial polishing agency. Unfortunately, the result was rather poor. The pitch could not be reduced to a layer thin enough to distinguish different features. Additionally, the fact that the polish equipment was normally used to polish much harder material had left stone dust, which caused severe scratches in the polished surface. It was clear that intensive collaboration with the company was required before it could produce an acceptable polished thin section from pitch. On the basis of this experience it was decided to continue the effort at the Department of Chemical Engineering at DTU. It was found that the department already owned polishing and microscopic equipment. It was further found that one of the laboratory technicians had prior experience in producing thin sections of coal and that he was willing to aid the project.

4.4.1.1 Preparation of Polished Thin Sections

A small lump of the pitch was obtained. It was slowly heated by placing it on a thin cover glass plate on top of a hot plate. Once the pitch had fully softened/melted and flowed out to a droplet of a thickness of approximately one mm it was removed from the heating source. It was separated from the cover glass by gently flushing it with water.

The plate of pitch was cut into a square with side lengths of approximately 1 cm. It was polished on one side by first grinding it on a rotating silicon carbide paper of grit numbers

1200 and 2400 followed by 4000. It was essential that the carbide paper and the sample were flushed with water during the grinding. The specimen was finally polished with lens tissue until a polished, carbonic surface was achieved. The use of lens paper is unorthodox for pitch polishing, but it was found necessary to polish the sample in this rather gentle way because the thin pitch layer was extremely fragile.

The polished side of the pitch was glued to a glass plate with methyl cyanoacrylate glue. The thickness was reduced by grinding it on silicon carbide paper grit number 500 and progressingly higher grit numbers. When the specimen was close to the required thickness it was polished as described earlier. The finished thin section had to be thin enough to allow light enter through it.

4.4.1.2 Results and Discussion

The sample chosen for polished thin section preparation was K18 (Figure 4-2). The reason was that this sample contained a relatively large amount of mesophase and would therefore yield information about the relationship between IP and mesophase. Figures 4-16 and 4-17 show a polished thin section of K18 in reflected and in transmitted light (polarized light). More mesophase spheres are visible in transmitted light and small spheres which are not visible in the reflected have emerged.

Two of the samples from the blended pitch study had not shown visible mesophase even though they had been manufactured including a thermal treatment at 410°C (Section 4.2.2). Figure 4-18 shows a thin section of the coal tar pitch. The primary QI particles of this sample are clearly visible and aggregation of the QI is observed. This indicates formation of embryonic mesophase but no spheres are visible even under higher magnifications. Figure 4-19 shows a polished thin section of the pitch which was produced from a thermally treated 50/50 blend of topped petroleum and coal tar. In this pitch the QI particles are clearly aggregating and even though the picture is taken under lower magnification the aggregates appear larger than in the previous sample. When the pitch is studied under the highest magnification (Figure 4-20), it is possible to observe small mesophase spheres covered with primary QI.

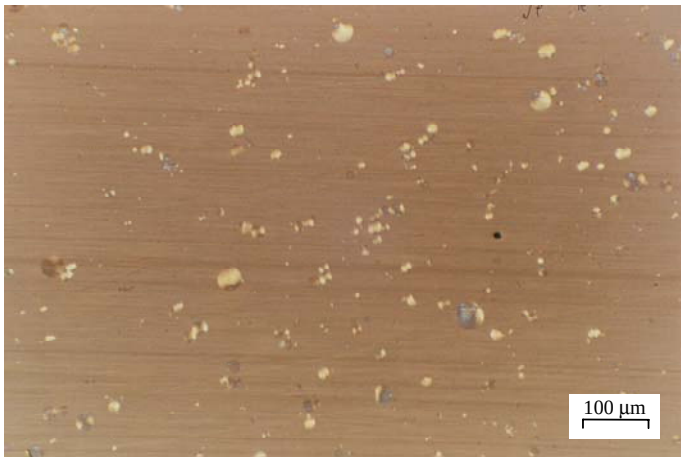


Figure 4-16: Polished thin section of K18, x100, reflecting light.

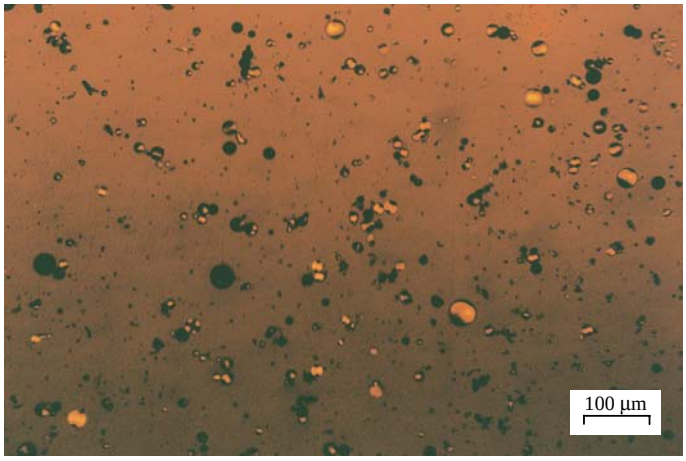


Figure 4-17: Polished thin section of K18, x100, transmitted light.

The method offered detection of QI aggregates as well as smaller mesophase spheres, but surprisingly there was no trace of IPs in any of the thin sections which were prepared. A plausible explanation is that the IPs were intimately connected to the polishing technique. To test this, the thin section which is seen in Figure 4-17 was very carefully polished on a cloth with 0.05µm alumina after which the IPs appeared in the surface.

Figures 4-21 to 4-24 show pictures of the alumina polished thin section with different light setting and use of filters. Figure 4-21 shows the thin section in reflected light with polarized filters. The IPs are clearly visible as dark shadows in the isotropic phase. Contrary to those observed in the pictures taken by RG (Figure 4-9), the IPs show a tail

following the polishing direction (downwards in the pictures). This is often observed in the petroleum pitches prepared for microscope in the Koppers Denmark laboratory. Figures 4-23 and 4-24 show the section in transmitted light, the first in polarized light and the second with crossed polarizing plates. The IPs are visible in these pictures as an irregular shape which is very similar to the one in Figure 4-9. Additionally, a dark trail of material is being extruded from the IP.

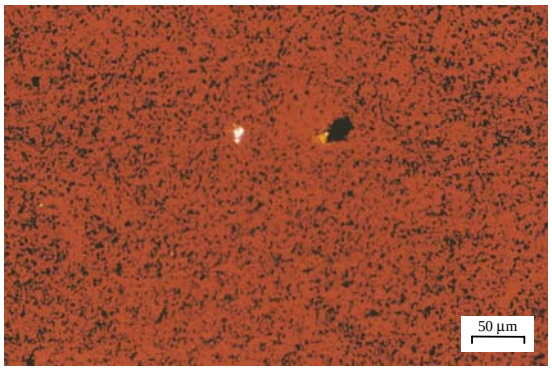


Figure 4-18: Polished thin section of TC7, x200, transmitted light.

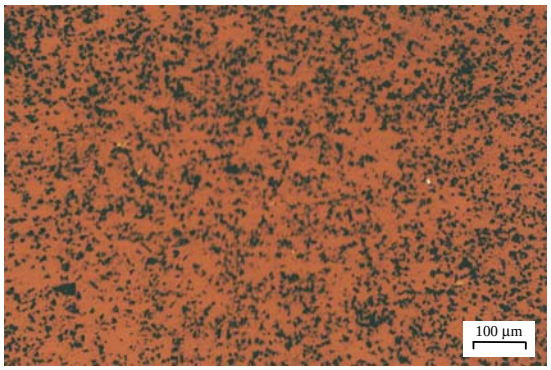


Figure 4-19: Polished thin section of TM3, x100, transmitted light.

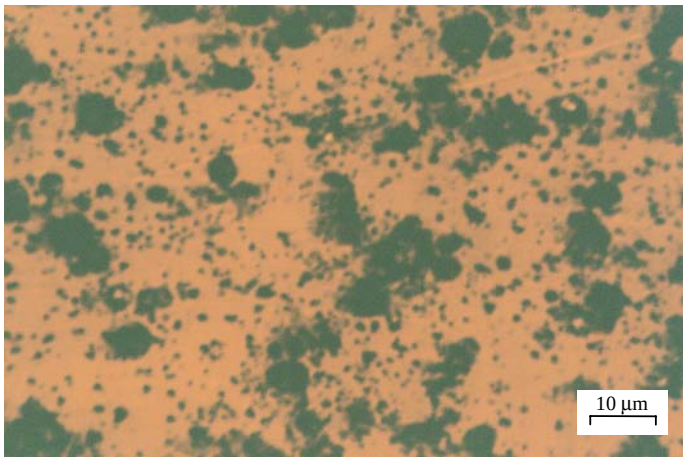


Figure 4-20 Polished thin section of TM3, x1000, transmitted light.

Figures 4-25 to 4-28 show the same area of K18 in different light and filter setting under a magnification of x200 while Figures 4-29 to 4-32 show another position of the pitch surface under a magnification of x400. Figure 4-28 is photographed in a dark field. In this lens, the light path is focused so out-of-plane objects are lighted up while objects in the

plane appear to be a black surface. The photography reveals a large amount of scratches in the surface of the sample, which are not visible in direct light. The mesophase spheres are not visible in the dark field while the IPs have become highly visible. This strongly indicates that the IPs have another hardness than the surrounding matrix.

A comparison between the pictures in Figures 4-21 to 4-32 gives a good indication of the nature of the irregular patch (IPs) which have been observed in the petroleum pitches. It seems that the isotropic phase of the petroleum pitch contains small pockets of material with a lower hardness and viscosity than the surrounding matrix. The significance of these pockets depends on when they have actually been formed. The patches are observed in the solidified pitch. The normal picture of solidification of pitch is that the viscosity of the liquid gradually increases during cooling which cause it to form an immobile glass at temperatures below the softening point. The appearance of the irregular patches, however, indicates that the isotropic phase is not as homogeneous as commonly believed. There are two plausible explanations for the nature of the IPs.

First, the IPs could be formed during solidification. As the temperature decreased the pitch matrix would become inhomogeneous. Molecular species with high melting points would be slowly separated from the liquid, forming domains with higher viscosity. As the temperature continued to decrease, the high-viscosity domains would slowly fill out the bulk of the isotropic phase, leaving small pockets of low-viscous liquid. The pockets would not be fully solidified at room temperature. At higher temperatures where the pitch became liquid, the isotropic phase would become fully homogeneous. In this case, the IPs would have no practical influence once the pitch had been heated to the temperatures where it is normally used.

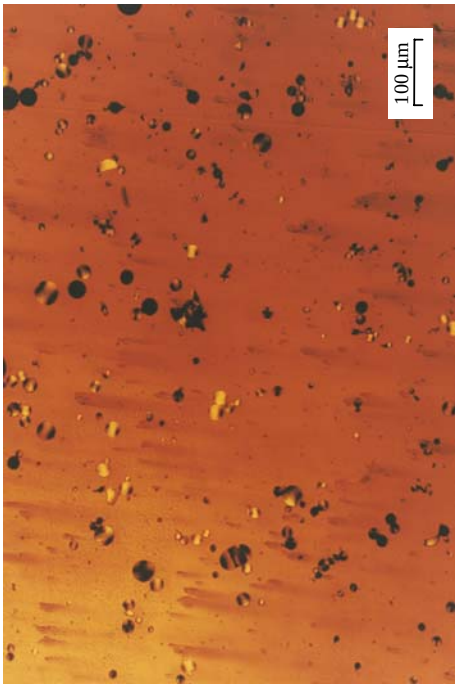


Figure 4-23: Polished thin section of K18, x100, transmitted light, no ¼λ-filter.

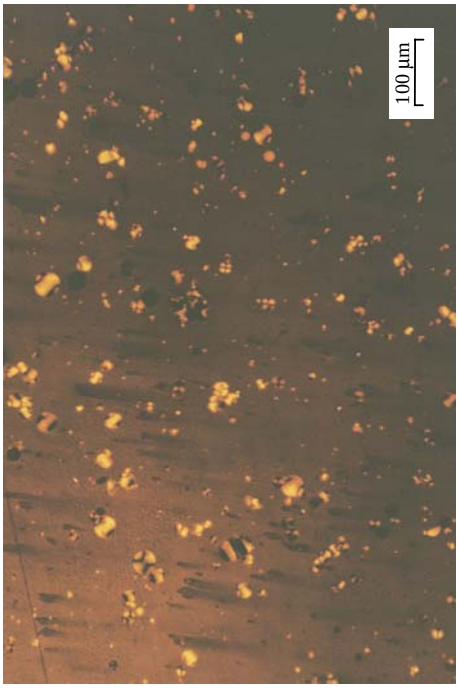


Figure 4-24: Polished thin section of K18, x100, transmitted light, with crossed polarizing filters.

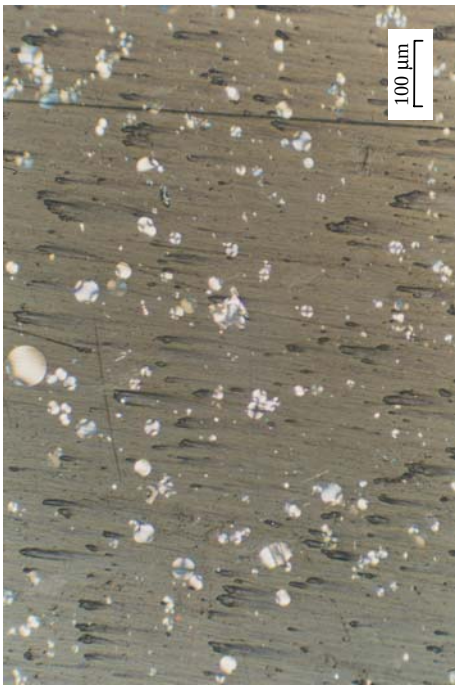


Figure 4-21: Polished thin section of K18, x100, reflected light, no ¼λ-filter.

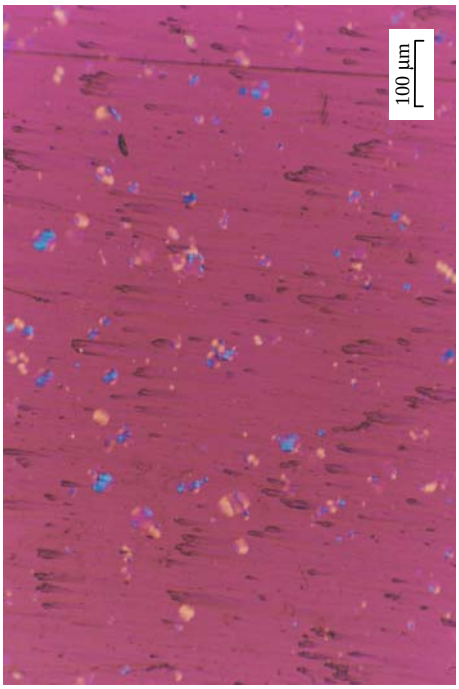


Figure 4-22: Polished thin section of K18, x100, reflected light, with ¼λ-filter.

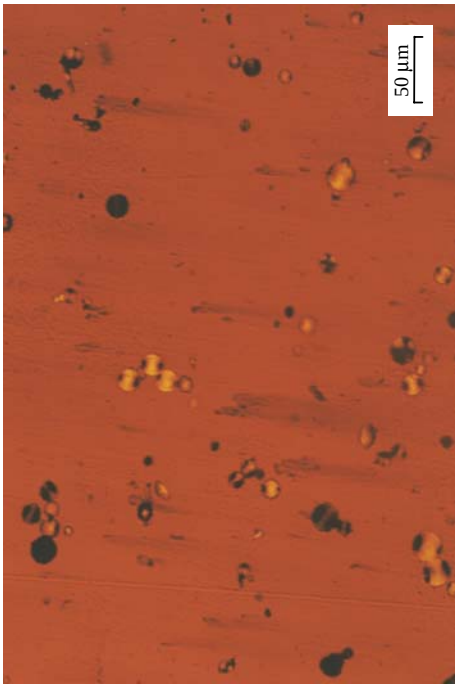


Figure 4-27: Polished thin section of K18, x200, transmitted light, no ¼λ-filter.

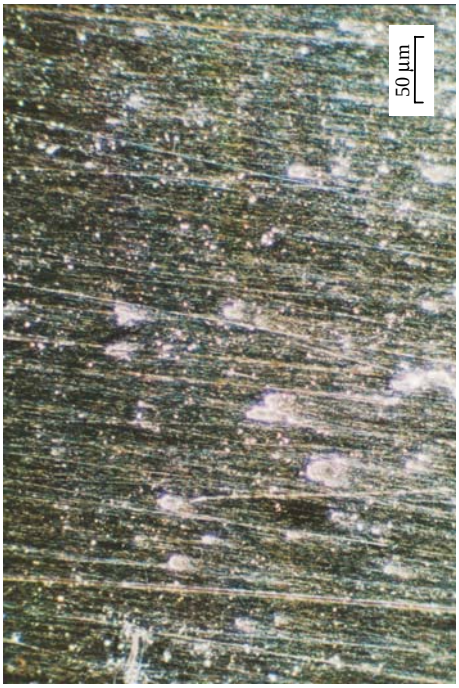


Figure 4-28: Polished thin section of K18, x200, reflected light, dark field.

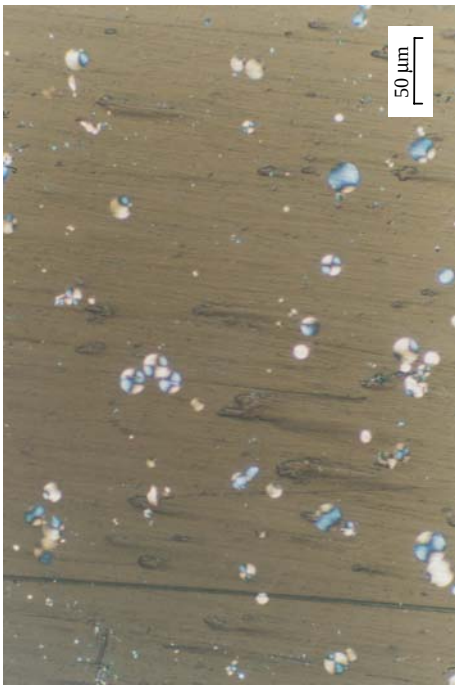


Figure 4-25: Polished thin section of K18, x200, reflected light, no ¼λ-filter.

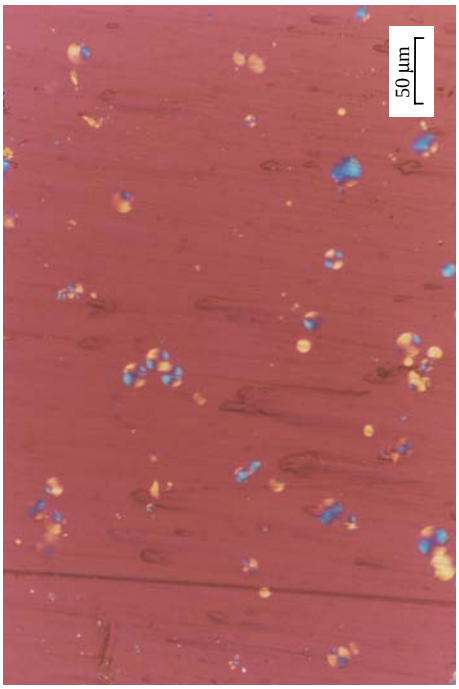


Figure 4-26: Polished thin section of K18, x200, reflected light, with ¼λ-filter.

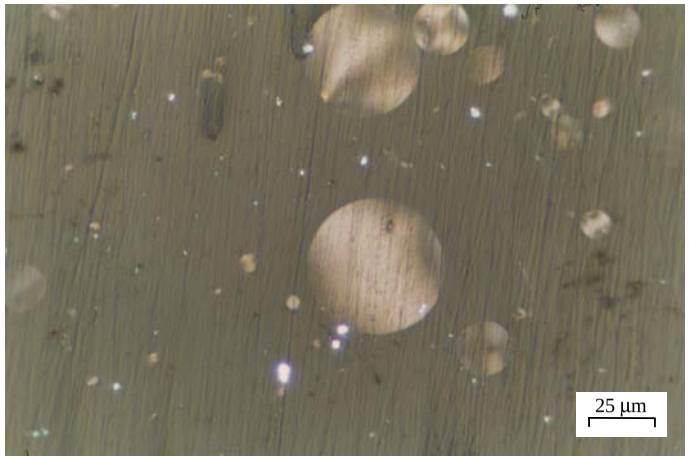


Figure 4-29: Polished thin section of K18, x400, reflected light, no ¼λ-filter.

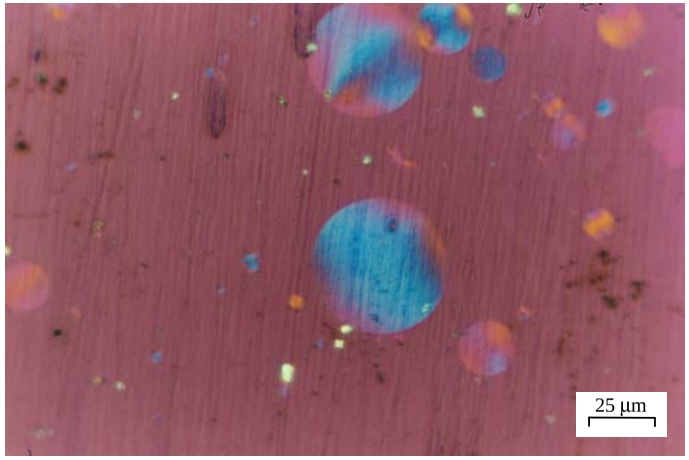


Figure 4-30: Polished thin section of K18, x400, reflected light, with ¼λ-filter.

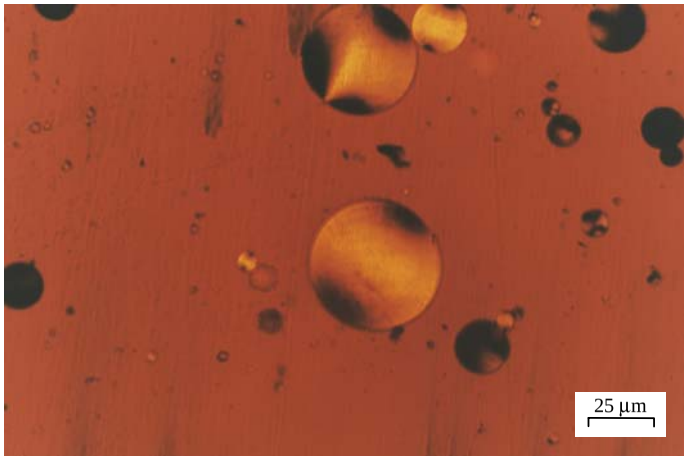


Figure 4-31: Polished thin section of K18, x400, transmitted light, no ¼λ-filter.

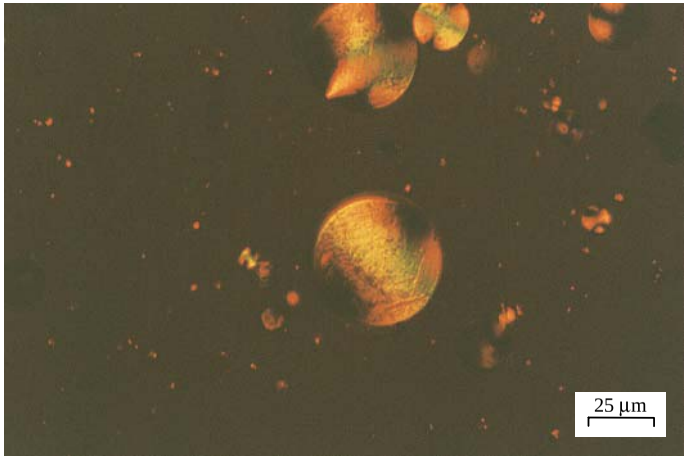


Figure 4-32: Polished thin section of K18, x400, reflecting light, with crossed polarizing filters and ¼λ-filer.

The second possibility is that the pitch was inhomogeneous at all temperatures. The inhomogeneity could be caused by different polarity or functionalities of the pitch components. In this case, the IPs would probably have a large influence on pitch performance under mixing and coking conditions. Since the IPs would be small pockets within the pitch of lower viscosity in the solid phase, they could be expected to have a lower boiling point leading to unwanted effects during binder pitch carbonization where fast expansion of the IPs could lead to a more porous carbon structure.

IPs have so far only been found in pure petroleum pitch. There have been no trace of the structure in coal tar pitch or in the blended materials. An interesting question is whether the IPs would appear in blended pitch. Two commercial pitch samples which have not been described earlier in this study, were received from Koppers Denmark. Blends with higher percentages of petroleum-derived material were made using these materials. The concentration of IPs was determined by the same counting procedure as described for mesophase (Section 4.2.1) and the "tail" was included in the IPs concentration. The concentrations are listed in Table 4-5. The IPs in the petroleum were large and easily detectable like those described earlier. When 5% coal tar pitch was added a few of the large IPs remained but the majority was now found to be of a very small size. When 10% CTP was added none of the large IPs remained, and as the concentration of CTP increased the size of the IPs decreased. At 50% coal tar pitch, a lot of very small IPs were still visible but the concentration could not be accurately determined due to the small size.

It seems that even small additions of coal tar pitch change the appearance of IPs and reduce the concentration of large IPs.

% CTP	0	5	10	25	50	100
% IP	0.11	0.28	0.30	0.27	-	-

Table 4-5: Concentration of IPs as a function of percentage of coal tar pitch in the coal tar pitch/petroleum pitch blends.

4.4.2. SEM

Parallel to the thin section study of the irregular patches (IPs) it was attempted to obtain SEM pictures of the structures.

The PP_{T1} sample which was prepared for the study described in Section 4.3 was sent to the laboratory of Marathon Ashland. Here it was analyzed by scanning electron microscopy/ energy dispersive spectrometry (SEM/EDS). Although very weak silicon and aluminum peaks were observed, SEM/EDS indicated that solids present in the sample were primarily carbon based. ICP analysis of the precursor tar and other petroleum pitches (Table 2-1 and Section 5.1.2) has always shown that the material contains very small amounts of aluminum (<8ppm). The metal peak therefore has to come from the alumina used for polishing. The amount of silicon in the pitch is not known but the fact that the pitch was ground on SiC paper might suggest that this material could also derive from the preparation. Since the peaks were described as weak the results were interpreted as meaning that the IPs contained mainly carbon material or elements of lower atomic numbers.

After having studied the IPs in more detail in the Koppers Denmark laboratory, it was decided to prepare a new sample (K18, see Figure 4-2) for SEM and submit it to examination by SEM at the Department of Physics, DTU. Figures 4-33 and 4-34 show SEM pictures of the sample. Figure 4-33 was recorded by a BSE (backscatter electron) detector. This type of detector does not show the contours of the surface but instead pictures are formed on the basis of the weight of the atoms in the subject. Elements lighter than carbon will appear to be dark while higher mass atoms will appear brighter. Figure 4-34 was recorded by a SE (secondary electron) detector, which shows the contours of the sample. The photographed area contains a hole (top, left corner) and it was therefore possible to find the exact same spot by use of the optical microscope. Figure 4-35 shows the area photographed in reflecting light with crossed polarized filters and a ¼ λ plate. The area to the right in the picture is seen to contain an area with coalesced mesophase, which is partly visible in Figure 4-34. Areas with IPs are black in this picture. When the dark

field utility of the microscope is applied (Figure 4-36) it is noted that the sample is very scratched, but IPs can be seen in the sample.

A large IP is seen a little to the left in the pictures. Figures 4-37 and 4-38 show an enlargement of this IP. Use of the BSE-detector makes it clear that the shape consists of small grains which mainly have elements of a higher atom number than carbon. Usually, the SEM laboratory in DTU would be capable of analyzing the exact atomic composition of the structures found in SEM analysis. Unfortunately, this unit broke down prior to the present analysis and it was not recovered in the course of the project. However, it seems reasonable to assume that silicon and aluminum would have been found as it was the case in the analysis of PP_{T1}.

On the basis of the SEM analyses of the IPs, it seems likely that they somehow cause SiC and alumina from the polishing tools to get stuck which sometimes makes them appear as hard grains in the surface. This is a plausible explanation for the natural QI particles, which were surprisingly found in the petrographic analysis of PP_{T1} (Table 4-3).

4.4.3. Conclusion on Irregular Patches

The irregular patches, which have been found in petroleum pitches, consist of pockets of less viscous material. During grinding and polishing this liquid is sometimes extruded from the original position. Additionally, it will sometimes pick up SiC and alumina grains during grinding and polishing.

4.5. Conclusion on the Microscope Study of Pitch

Little or no mesophase was found in the pitches produced from thermally treated, topped tars. 385°C was the lowest treatment temperature where mesophase was detected in the resulting pitch. The actual concentration of mesophase was in all cases lower than the concentration of secondary QI, but no direct relationship could be determined.

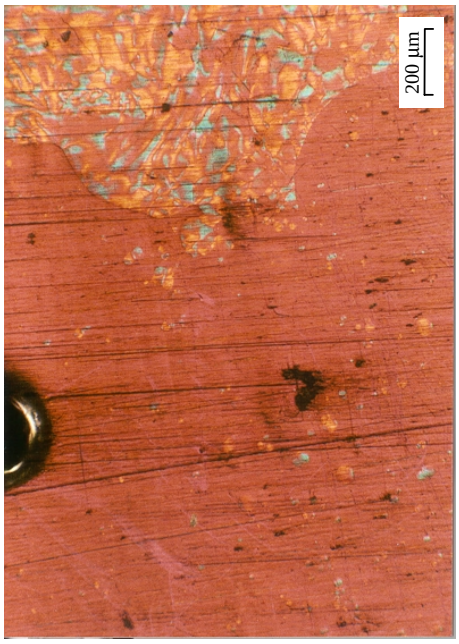


Figure 4-35: Optical microscope picture of K18, x50, reflected light, ¼λ-filter.

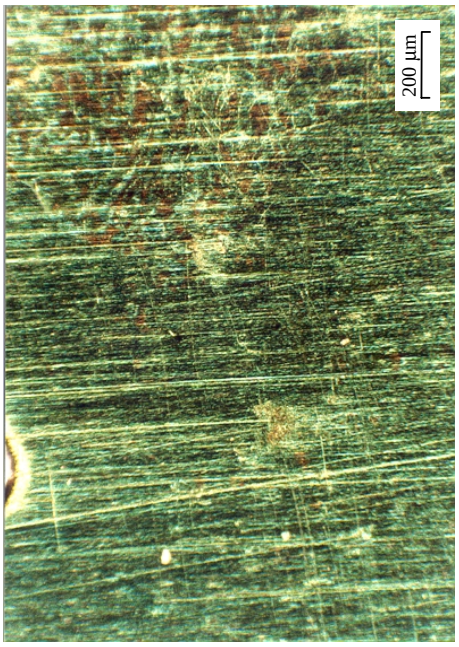


Figure 4-36: Optical microscope picture of K18, x50, reflected light, dark field.

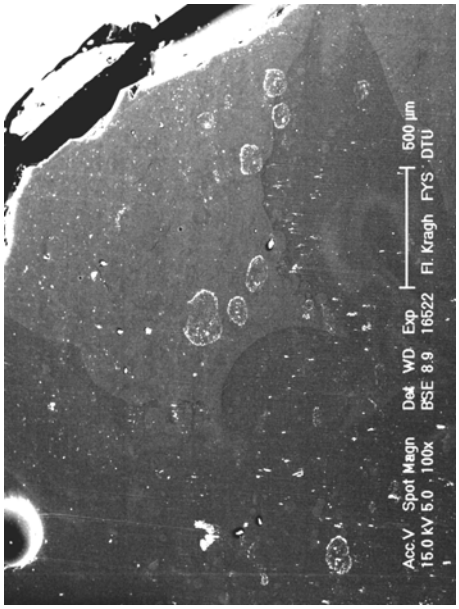


Figure 4-33: SEM picture of K18. x100, BSE-detector.

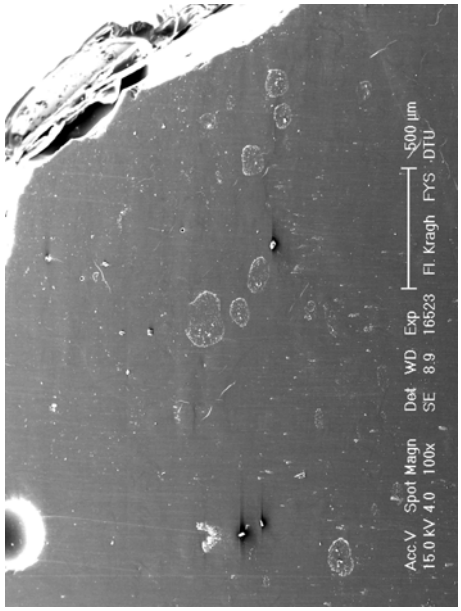


Figure 4-34: SEM picture of K18. x100, SE-detector.

Figure 4-39: Optical microscope picture of K18, x400, reflected light.

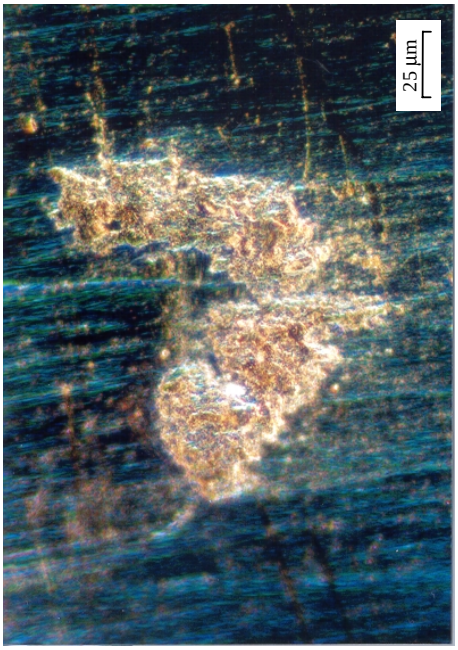


Figure 4-40: Optical microscope picture of K18, x400, reflected light, dark field.

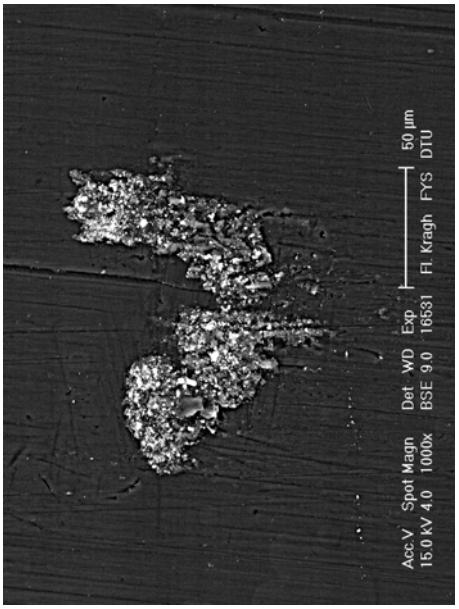


Figure 4-37: SEM picture of K18. x1000, BSE-detector.

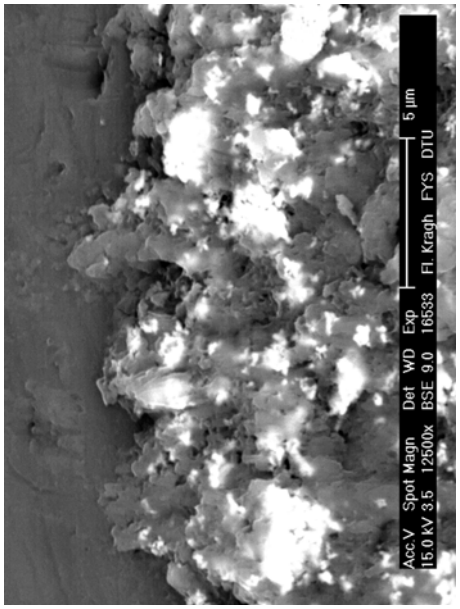


Figure 4-38 SEM picture of K18. x12500, BSE-detector.

The general tendency was that the concentration of mesophase was higher with higher treatment temperature. There was no clear influence of the percentage of coal derived material in the pitch but generally the petroleum material seemed to form mesophase more readily than the coal tar material.

The samples manufactured for the anode study were analyzed by the Ralph Gray services. It was found that all the pitches show evidence of being thermally treated. Some of the samples have detectable levels of mesophase, but the sphere sizes are close to or below 4 μm, which is the detection limit set by the ASTM 4616-95 standard. Additionally, it was confirmed that a homogeneous blend of coal and petroleum material has been obtained.

In the petroleum pitches, some irregular patches are observed. The nature of these patches has been found to be pockets in the isotropic phase containing less viscous material. During polishing, the IPs had a tendency to pick up polishing alumina and grains from the laps. The appearance of IPs is only observed in petroleum pitch and materials which predominantly consist of petroleum pitch. The influence of the inhomogeneity in the isotropic phase is not known.

5. Analytical Approach to Tar and Pitch

In the present study of thermal treatment in the manufacture of pitch, a number of different analysis techniques were applied in order to gain further information on the feedstock materials as well as on the thermal treatment process. The scope of these analyses was to obtain an understanding of the chemical nature of the modifications introduced by the thermal treatment. Some of the attempts were partially successful but, generally, they suffered from the fact that tar and pitch consist of thousands of different components. The mild thermal treatment only results in minute changes in material, which means that high sensitivity is required. This chapter summarizes analyses which were used to gain further understanding of the thermal treatment process and the materials used in the process.

5.1. Composition of Pitch

5.1.1. Elemental Composition

It was investigated whether thermal treatment influenced the basic atomic composition of the resulting pitch. The elemental composition was determined on selected pitch samples by the commercial analysis laboratory, DBLab. The content of carbon, hydrogen, nitrogen, sulfur and in some cases oxygen was measured and the data is listed in Appendix E. According to the laboratory, the measurement precision of the method was dependent on the relative content but they guaranteed C, H, and N to be determined with an accuracy of ±1% and O and S with ±3% absolute. Based on the data the accuracy is probably better than stated, but the uncertainty was underlined by the fact that negative content of oxygen was calculated by difference.

The elemental composition of the precursor topped tars is given in Table 2-1. A comparison of the results obtained for the topped tars and the pitches shows that the hydrogen content is lower in the pitches than in the tars. This result is well known and is interpreted as a higher condensation of the aromatic ring structures in the pitch. The nitrogen content and the sulfur content are of the same magnitude for the two materials

even though there is a tendency of higher nitrogen content in the pitch. The pitches where the oxygen content was analyzed, show higher oxygen content in the pitch than in the topped tar. This could be interpreted as if the components which were removed during the process had a low oxygen content. It is, however, also possible that a weak oxidation of the material has occurred despite the precautions. The increase is highest in the petroleum-derived material while it is more moderate in the pitches containing coal-derived material.

In order to compensate for the uncertainty of the elemental analysis, atomic ratios of hydrogen and the heteroatoms relative to carbon were calculated. The ratio tells how much of the given atomic element the pitch contains relative to atomic carbon. Especially, the H/C can be used to deduct information about the material. For long-chained aliphatic components H/C is equal to two ($(CH_2)_\infty$). For a benzene ring H/C equals one while the value is less than one for larger aromatic ring systems. The calculated ratios are listed in Appendix E and the results for H/C, N/C and S/C are plotted in Figures 5-1 to 5-3.

The hydrogen content is higher in the petroleum-derived pitches than in the coal tar pitches (Figure 5-1). This relationship was expected on the basis of literature references. The hydrogen content found in the coal derived material is almost unaffected by the thermal treatment, while a clear decrease with increasing thermal treatment temperature is observed for the petroleum pitch. This decrease can be interpreted as loss of aliphatic side chains.

The nitrogen content in the pitch is unaffected by the thermal treatment (Figure 5-2). Due to the high uncertainty of the measurements, it is not possible to interpret the tedency of the oxygen content and the sulfur content (Figure 5-3). Based on the present data the content of heteroatoms in the pitch is expected to be more or less unaffected by the thermal treatment of the topped tar. The content is, however, rather low in the treated materials, meaning that the effects might not be detectable.

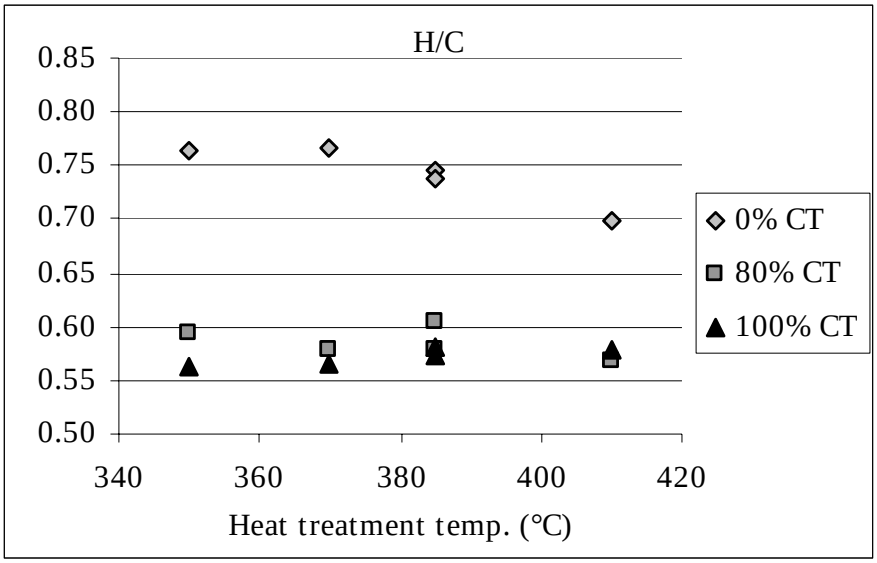


Figure 5-1: Molar H/C as functions of heat treatment temperature. Legend: percentage of coal tar material in topped tar prior to thermal treatment.

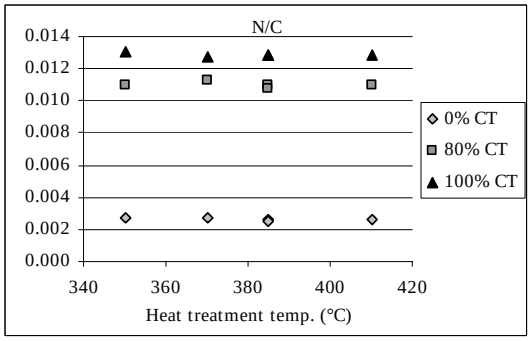


Figure 5-2: Molar N/C as functions of heat treatment temperature.

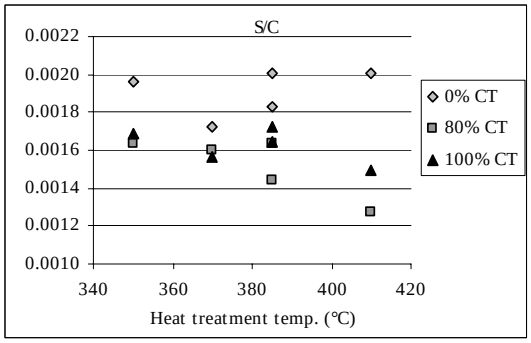


Figure 5-3: Molar S/C as functions of heat treatment temperature.

5.1.2. Inclusion of Minerals

Coal tar pitch contains trace amounts of minerals. These components derive from the carry over QI and originate directly from the coal (see Chapter 4). The traditional method of getting an indication of the metal content is to reduce a pitch sample to ash and in this way estimate the mineral content. In this work, the metal content in the pitches was measured by use of an ICP spectrometer (Inductively Coupled Plasma Optical Emission Spectrometer, Optima 3000 DV, Perkin Elmer). Sulfur, aluminum, calcium, iron,

magnesium, manganese, sodium, nickel, lead and zinc were analyzed in the pitches produced from blended feedstocks and the results are found in Appendix F.

The results show that the metal content in the pitches is strongly correlated with the amount of coal-derived material in the feedstock. The petroleum-derived pitches are almost free of metal ions. There is no significant effect of the thermal treatment and the actual amount of metals seems unaffected by the pitch preparation method.

Moreover, the content of sulfur was analyzed. The sulfur is probably found within the aromatic molecules rather than it exists in inorganic form in the carry over QI. The content which was found by the use of ICP was generally a little higher than the content found by the elemental analysis (Figure 5-4). The sulfur content of the petroleum pitches was generally a little higher than the content found in the coal tar pitches. It was still not possible to detect any influence from the thermal treatment.

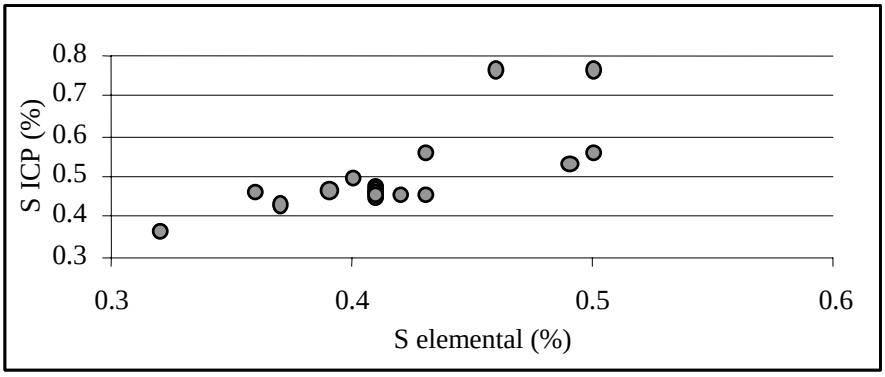


Figure 5-4: The sulfur content in the pitches measured by ICP as a function of the content found by elemental analysis.

5.2. GC of Volatile Components

One of the important issues of this work is what happens to the pitch at a molecular level as a result of the mild thermal treatment. It soon became clear that this question could not be readily answered. The abundance of components made it difficult to track individual routes of reaction. Additionally, the exact composition can only be obtained of the most

volatile fractions of the pitch. The following section aims at finding out what happens to the components which can be analyzed.

The effect of the thermal treatment was accessed by analyzing the oil which was distilled off a thermally treated topped tar and a non-thermally treated topped tar in order to produce pitch. The starting material consisted of the two topped tars (F98017A and F98020), which had been received as topped from the Koppers Denmark plant (see Section 2.2.1). The two materials were first distilled directly into pitch and the oils were collected for GC analysis. New topped tar samples were given a thermal treatment at 385°C for six hours (for a detailed description, see Chapter 2.2.2). The treated topped tars were distilled into pitch and the oils collected. The properties of the pitches are given in Table 5-1.

Pitch		Straight dist. coal tar pitch	Straight dist. petroleum pitch	Heat-treated coal tar pitch	Heat-treated petroleum pitch
Code		200	201A	202	203
Pitch yield		47.2	60.2	54.5	55.0
SP	(°C)	135.6	109.0	130.8	126.3
QI	%(w/w)	8.1	0.4	7.5	1.2
TI	%(w/w)	27.7	-	31.2	23.8
CV	%(w/w)	64.0	44.2	63.0	55.8
Mesophase	%(v/v)	0.02	-	0.04	0.06

Table 5-1: Analytical properties of the pitch.

The oils were analyzed by GC and GC-MS (the chromatographic conditions are listed in Appendix G). It was determined which components were appearing and which were being removed by GC. The peaks were then later identified by GC-MS. The software for the GC-MS contained a library of mass spectra which were compared with the spectra of the individual peaks. Based on this comparison and the boiling points of the suggested components (by Anderson et al., 1963), identification was made. The identified components and their retention times are listed in Appendix G.

GC of the oil obtained from the untreated topped coal tar revealed that a sharp distillation cut had been obtained at the component naphthalene. The oil contained trace amounts of naphthalene and no lighter components were present. The sample exhibits the well-known coal tar “finger print”. The composition of coal tar pitch shows only minor variations when

coal tar pitches derived from various coal sources are compared. Blanco et al., 1991, gave an excellent example of a full characterization of a coal tar pitch.

The oil which was distilled off the thermally treated topped coal tar showed an increased amount of volatile components. Components being eluted prior to naphthalene had been formed within the material which now showed traceable amounts of phenol, indan and creosol along with increased amounts of naphthalene. There was a general increase in components with one or two aromatic rings as well as methylated PAHs (polyaromatic hydrocarbons). These components are probably formed during decomposition of larger molecules interconnected with aliphatic bridges. Another distinct group which was formed was the hydrated PAHs like indan and 9,10 dihydroanthracene. These components are formed when a PAH acts as a hydrogen acceptor (Section 1.1.2). The concentration of anthracene was too high for a decrease to be detected due to the limited decrease compared with the total content.

The components consumed during the thermal treatment fall into two groups. First, aromatic groups interconnected by a single bond, i.e. biphenyl and phenylnaphthalene, were consumed as a result of the thermal treatment. This can be explained either by a hydrogen donor/acceptor theory or by a further cross-linking theory. The second group which showed a decrease was PAHs containing nitrogen or sulfur atoms in the aromatic ring structure like quinoline, acridine and benzo-naptho-thiophenes. It is not possible to determine the fate of these components. Based on the elemental analysis (Section 5.1.1), the components are neither being removed nor being incorporated into larger molecular components in relatively higher amounts.

The chromatograms of the oil obtained from the topped petroleum tars were more difficult to interpret. These materials contained an abundance of mono-, di- and trimethylated and ethylated components along with other side-chain-containing components yielding chromatograms crowded with peaks. The chromatogram of the oil obtained from the untreated topped petroleum tar revealed that the cut point of the topping distillation had indeed been lower than that found for the coal tar (as stated in Section 2.2.1). As seen for the coal tar, thermal treatment led to formation of volatile components. It was possible to

detect a reduction in ethylated and trimethylated components. Moreover, the concentration of anthracene was so low that a clear decrease could be observed. Unfortunately, the 9, 10, dihydroanthracene eluted in an area with an abundance of other peaks so it was not possible to detect a clear increase. An oil from an 80/20 blended, thermally treated topped tar was additionally analyzed but because of the difficulties in analyzing the petroleum material, it was not possible to make any conclusions based on this chromatogram.

In the analysis of the oils obtained from the thermally treated topped tar trace amounts of the more volatile components, like toluene, phenol and creosol, were found. During the thermal treatment components in gas form under reactor condition were allowed to leave the reactor into the purge stream (see Figure 2-6). In one experiment, this purge stream was led through a cold finger submerge in an acetone/CO_2 bath. The experiment was a thermal treatment of a 90/10 blend of topped coal and petroleum tar at 410°C for six hours. After the thermal treatment the cold finger was rinsed with 10 ml dichloromethane and this solution was analyzed by GC. The chromatogram showed that high amounts of toluene had been condensed from the gas stream. Additionally benzene, ethylbenzene, naphthalene and methylnaphthalene had been formed in high amounts along with several other tar components in the same boiling range. The heaviest component found in the condensate was fluoranthene.

The GC analysis reveals that volatile components are formed during the thermal treatment. The appearance of these components indicates that larger molecules, which are bound together by single bonds or aliphatic bridges, are being split up. Moreover, it is observed that molecules which can act as hydrogen acceptors (like anthracene) react to their hydrogenated form. This indicates that polymerization and further condensation of ring structures takes place in the fractions which cannot be analyzed by GC. A reduction in components containing heteroatoms in the ring structure is observed but based on the present results, it is not possible to suggest the actual reactions.

5.3. Spectroscopy

The following section describes the application of infrared spectrometry (IR) and nuclear magnetic resonance (NMR) to pitches produced by thermal treatment. The two methods are generally known to yield information about functional groups within the molecules.

5.3.1. IR Analysis

Infrared (IR) spectrometry detects the vibration and stretching of molecular bonds within organic molecules. In the analysis of pitch, the method is generally used to determine the aromaticity. The method is, however, capable of revealing further information. Guillén et al., 1992, gave a very thorough description of FTIR analysis of pitch and solvent fractions of pitch.

The definition of aromaticity (I_a) which has been used is given by Equation 5-1. The calculation is based on C-H bond stretching of H atoms attached to aromatic rings (3050 cm^{-1}) or aliphatic groups (2920 cm^{-1}).

$$I_a = \frac{Abs_{3050}}{Abs_{3050} + Abs_{2920}} * 100\% \qquad \text{Equation 5-1}$$

I_a	Aromaticity
Abs_{3050}	Absorbance of 3050 cm^{-1} band
Abs_{2920}	Absorbance of 2920 cm^{-1} band

The measurement was adopted from an internal Koppers Denmark method. The aromaticity was measured on the carbon tetrachloride soluble part of the pitch and the measurement was conducted in solution. Abs_{3050} was estimated as the integrated area between 3000 and 3100 cm^{-1} and Abs_{2920} as the integrated area between 2800 and 3000 cm^{-1}. It should be noted that this approach is highly simplified and will generally yield I_a values which are too low. By using area instead of peak heights, hydrogen in CH_2 and CH_3 values is counted more than once.

The aromaticity of the topped coal tar (F98017A), which was used for thermal treatment of blended pitches, was found to be 61% while the topped petroleum tar had an aromaticity of 27%. This confirms the expectation of the coal-derived material being more aromatic than the petroleum-derived material.

In the study of petroleum pitches, produced by thermal treatment of topped tars at different temperatures (Section 2.3.1), the aromaticity of the resultant pitches was measured. Figure 5-5 shows the increase in aromaticity with increasing severity of the thermal treatment. The aromaticity shows a limited increase until a treatment temperature of approximately 390°C. The measurement supports the general tendencies described in Chapter 2.

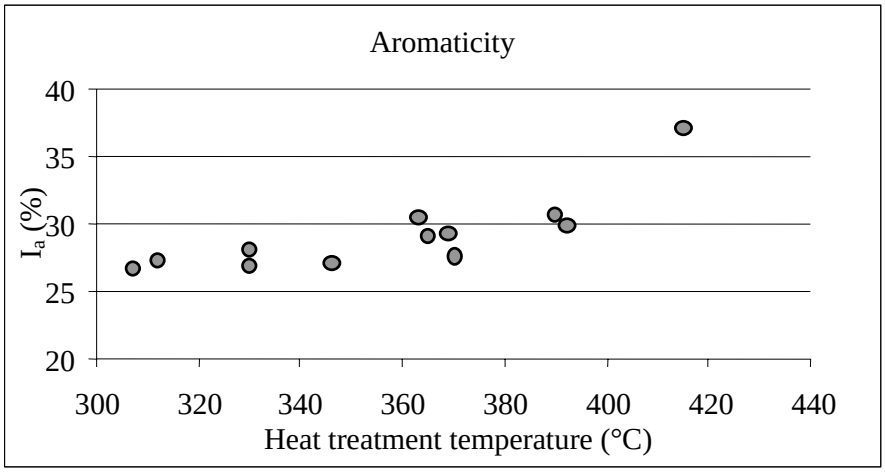


Figure 5-5: Aromaticity of petroleum pitch as a function of thermal treatment temperature.

5.3.2. NMR Analysis

Nuclear magnetic resonance (NMR) spectrometry is an important tool for obtaining data on how hydrogen or carbon atoms are bonded within the molecules. Typically, ^{1}H NMR has been used. In pitch research, this method has the drawback that the hydrogen content in the pitch fractions is typically low (Figure 5-1) and that the aromatic structures are not well represented. Besides, the equipments require that the sample is dissolved in a deuterium rich solvent, so that only the soluble part of the pitch is actually analyzed.

^{13}C NMR offers an analysis based on the bonding of carbon atoms, giving information on the larger molecules in the pitch. Recently, new understanding of the toluene insoluble part of the pitch has been obtained by Andrésen et al., 1998a, 1998b and 2000. This research indicates that the toluene insoluble fraction remains relatively unchanged by thermal treatments as it has average molecular sizes of approximately nine to ten aromatic rings.

It was investigated whether ^{13}C NMP could yield new understanding concerning the processes studied in this work. Three pitches were sent for analysis at Western Research Institute, Laramie, USA. The pitches were chosen from the experiments with pitch produced from blended coal- and petroleum-derived material thermally treated at 385°C. The pitches produced from 0/100, 80/20 100/0 blends of topped tars were chosen (see Section 2.3.3 for further information on the materials) and analyzed by cross-polarization (CP/MAS) and single-pulse (SP/MAS) excitation techniques.

Based on the ^{13}C NMR the aromaticity was calculated (Table 5-2). The aromaticity of the coal-derived pitch is generally found to be higher than the aromaticity of the petroleum-derived pitch. This result was expected and it is well in line with previous results. Generally, SP/MAS spectra are more quantitative than CP/MAS spectra. However, the aromaticities of the SP/MAS spectra are lower than those of the CP/MAS mass spectra. This is a little surprising because it is the exact opposite of the general tendency found by Andrésen et al., 1998b.

Sample	% coal material	CP/MAS	SP/MAS
TP4	0	0.83	0.74
TM11	80	0.93	0.90
TC6	100	0.96	0.91

Table 5-2: Aromaticity measured by ^{13}C NMR. Pitches manufactured from topped tar thermally treated at 385°C

The spectra obtained for the samples were quite featureless and revealed that the samples consisted of large aromatic carbon components, probably consisting of condensed rings and small aliphatic side groups. A shoulder at ~140 ppm was most clearly observed in the CP/MAS spectrum of TP4 and this peak is attributed to alkyl substituted aromatic carbon.

The petroleum pitch (TP4) shows a larger peak at ~20 ppm than the two other pitches. This peak is probably due to methyl carbons. All of the pitches have a relatively low content of methylene carbons (~30 ppm), indicating short side chains.

Based on the ^{13}C analysis, the pitches can be said to consist of large aromatic carbon components and the petroleum-derived material to have a higher percentage of side chains than the coal-derived pitch. It is possible to detect a difference between the pure coal tar pitch and the 80/20 blended pitch but the spectra show great similarities. On the basis of the results it was doubted whether the method would be sensitive enough to detect actually the difference between the treatments which were applied in the present study. If a larger number of spectra had been recorded on a wide array of pitches and their fractions, it is possible that the method would have yielded a new understanding of the process. The test performed here did, however, make it clear that it was not possible to approach the subject by a limited study.

5.4. Discussion of the Analytical Approaches

It has been part of the scope of this project to obtain an understanding of thermal treatment at a molecular level. In the present chapter as well as in Chapters 2 and 3, analytical data measured on the products of the experiments has been presented. Even though the data yields some information about the process, a full understanding of the chemistry has not been revealed. It is appropriate to consider the reasons why this understanding could not be obtained.

The first and most pronounced problem is the abundance of components contained in the pitches and tars. It is literally impossible to anticipate all the types of reactions a certain molecule could participate in. In addition, some of the only methods which are capable of detecting separate molecules are GC and HPLC and these methods are limited to the volatile or highly soluble part of the pitch. This leaves the heavier components largely uncovered. SEC analysis can provide information about the heaviest components in the pitch but further knowledge of the composition and the molecular weight is still required.

Spectroscopic methods like IR and NMR are capable of giving bulk characterization of the pitch. The methods, however, have certain drawbacks when very small modifications are studied. Spectroscopic methods require experience and a good understanding of the theory that is not easily obtained during a limited study. Inspired by the works of Andrésen et al, it might be an idea to fractionate the pitches prior to analysis.

Another more unfortunate problem is the experimental approach used in this project. Since the project has had a large industrial scope the focus has been on the resulting product, namely pitch. While it offered a better understanding of the practical significance of the processes, it implied additional requirements of the interpretation of the analytical results as well. The problem is illustrated in Figure 5-6, which is produced on the basis of experimental data but is slightly modified to aid the discussion. The pitches were produced by different combinations of thermal treatment and distillation.

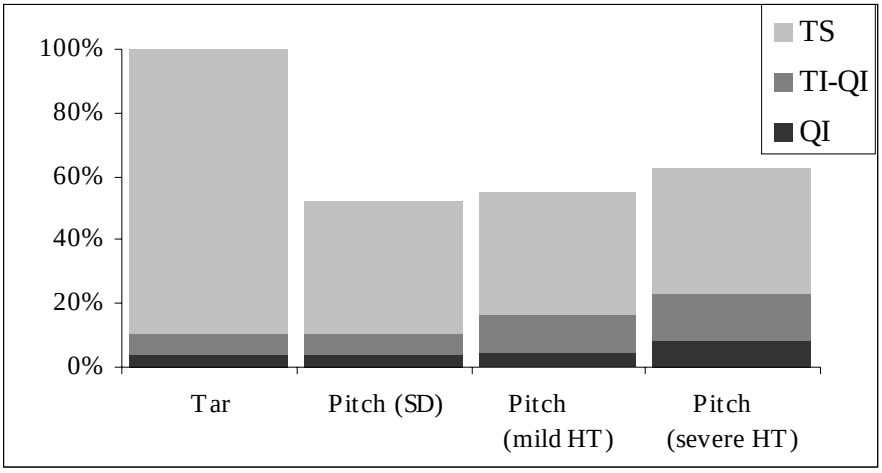


Figure 5-6: Solvent fractions of tar, pitch manufactured by straight distillation and 120°C softening point pitch manufactured from thermally treated topped tar. (SD: directly distilled, mild HT: produced from thermally treated tar with no secondary QI in the pitch, severe HT: produced from thermally treated tar with secondary QI in the pitch).

Figure 5-6 shows that the thermal treatment resulted in an increased amount of components in the heavier solvent fractions. Since the softening point was maintained at 120°C, this increase had to be balanced by an equally higher content of lighter component. In Figure 5-6 it is illustrated how the thermal treatment moves previous quinoline and toluene soluble compounds to be included in the insoluble fractions. Thus, compounds are moving

from one solubility class to another. Additionally, compounds which would otherwise be removed by distillation now remain in the pitch. Because of the large array of components within the pitch, it is reasonable to perform some fractionation prior to further analysis because this focuses the analysis on a certain class of components. Unfortunately, it is difficult to interpret the significance of a changed characteristic of a fraction as this can be attributed either to a true alteration of the molecules or to the fact that it is simply not the same material which is analyzed.

5.5. Conclusion on the Analytical Approaches

Thermal treatment of topped tar causes side chains to be broken off the aromatic cores. Smaller molecules are hydrogenated indicating polymerization and further condensation of aromatic rings in the heavier fractions of the pitch. Petroleum-derived material is less aromatic than coal-derived material, which means that this material is capable of undergoing larger changes than the coal-derived material before actual carbonization reactions take place.

6. Anode Study

6.1. Introduction

The purpose of this part of the work has been to test how different types of pitch perform in bench scale anodes for aluminum smelting. The work described previously in this thesis was focused on thermal treatment of topped tar and evaluation of the pitches. The evaluation was based on analysis of the pitch, like yield, softening point (SP), solvent insoluble fractions (toluene insoluble (TI), quinoline insoluble (QI)) and coking value (CV). These physical characteristics of pitch might not give a proper and complete picture of the actual performance of the pitch when diverse precursor materials and treatments are applied. In this part of the study the pitches were tested in a situation imitating industrial use of the product within practical limits.

6.2. Raw Materials

6.2.1. Pitch

The study focused on two parameters: 1) Thermal treatment in the manufacture of pitch and 2) the performance of petroleum-derived pitch and dual-origin pitches. The preparation of the experimental pitches and the anode study were rather time- and resource-consuming so that only a limited number of pitches could be tested.

In order to limit the size of the study it was decided to make two series of binder pitches: One where topped tar was straight distilled into pitch and another where topped tar received a thermal treatment prior to the final distillation. The experimental treatment of the pitches was chosen on the basis of the results which were obtained in Chapter 2. It had been found that treating the topped tar at 385°C made it possible to produce a pitch just on the edge of forming mesophase. It was decided to use this temperature in order to utilize the severest treatment possible which did not actually result in mesophase.

To complete the experimental plan, pitches derived from coal tar and petroleum materials in combination were used. In Chapter 2, it was indicated that there was no interaction between the two materials during thermal treatment. This was further investigated by using two combination routes. The first route was to produce two separate products and blend them as finished pitches. The other method was to blend the topped tars and process the two materials together, as it had been done in Chapter 2. The straight distilled pitch was only combined as pitch. Table 6-1 gives an overview of the experimental plan and the codes assigned to the pitch types. All the pitches were manufactured from the topped tars (F98017A and F98020), which have previously been used for the thermal treatment (Table 2-1).

Blend	Treatment	Coal tar	Blend 80/20	Petroleum tar
Blended as pitch	Straight distilled	CTP_S	MIX_S	PP_S
	Heat treatment	CTP_{T1}	MIX_{T1}	PP_{T1}
Blended as topped tar	Heat treatment		MIX_{T2}	

Table 6-1: Experimental plan for the manufacture of pitch.

6.2.1.1 Production of Pitch

The production of the pitch took place in equipment similar to the one described in Chapter 2. In order to produce larger quantities the equipment had been scaled up. The thermal treatment took place in a larger pressurized container which had been designed to hold a five-liter beaker. The beaker was filled with approximately four kg of topped tar and the heat treatment took place using the same oven as depicted in Figure 2-6. Apart from the size, the treatments only differed by the fact that there was no stirring during thermal treatment. When the thermal treatment was completed, the topped tar was transferred to a ten-liter, three-neck distillation flask where it was distilled into a 120°C softening point pitch. Ten kilograms of each of the seven pitches from Table 6-1 were produced. The properties of the resulting pitches are given in Table 6-2. It was found by optical

microscopy that MIX_{T1} and MIX_{T2} had been homogeneously blended at a microscopic level and that all non-straight distilled pitches bore traces of thermal treatment (Chapter 4). The analytical values did not indicate that the severity of these treatments had been larger than that previously described (Chapter 2).

	CTP_S	PP_S	MIX_S	CTP_{T1}	PP_{T1}	MIX_{T1}	MIX_{T2}
SP (°C)	117.3	119.2	117.4	119.1	118.0	119.7	117.5
QI (%)	6.8	0.4	5.6	7.1	0.9	5.7	4.6
TI (%)	23.0	10.3	19.8	29.3	21.1	27.4	25.8
CV (%)	57.7	47.2	55.1	59.1	53.7	58.7	57.3
Ash (%)	0.19	0.01	0.13	0.20	0.01	0.16	0.11
Dens. (g/cm^3)	1.312	1.208	1.289	1.319	1.235	1.304	1.287

Table 6-2: Analytical properties of the pitches.

6.2.2. Coke Blends

The aim of this study was to investigate the different pitch types. For this reason it was chosen to use a coke mix which had already been used for a number of studies at the Koppers Research Center in Harmarville, USA, and not to engage in a more detailed study of the coke. The materials, consisting of calcined coke and butts, were obtained from a commercial aluminum producer.

The calcined coke as received was screened into three size fractions: coarse, intermediate and fine. The coarse coke ranged in size from 0.3 cm to 5 cm, the intermediate coke ranged from 0.3-0.08 cm and the fine was less than 0.08 cm. In the coke blends, a fraction called anode butts was included. The butts are a recycled fraction of used anodes and they are a part of most industrially produced anodes. The fraction is known to have a significant effect on anode properties. Unused remains of anodes are cleaned and crushed to a convenient size. The size of the butts ranged from 1.5 cm downwards.

Coke mixes were prepared in 13 kg batches by use of a commercial recipe. This recipe had been used for previous studies in the Harmarville Technical Center and was considered the

standard coke blend of the facility. The composition is known by the author but will not be listed here. One entire 13 kg batch was used in each lot of green mix.

6.3. Production and Testing of Anodes

In order to produce the best possible anode from a given pitch, the recipe and the manufacturing conditions must be optimized. This involves a long process where the effect of coke blend screens, pitch level and processing temperature and duration can be investigated. Whether or not the optimum condition has been obtained for a given set of raw materials has an enormous influence on the quality of the anodes. This is particularly true of such different binder pitches as in the present study. The ideal procedure would have been to optimize the composition of the coke blend, find the responding binder level for each of the pitches and examine the influence of mixing and forming conditions as well as the bake profile. This would, however, have been extremely time-consuming and it was beyond the scope of this work. Additionally, the quantities of pitch required would be impractical. It was therefore decided to use one coke blend and set of manufacturing conditions for all the anodes and not attempt to optimize it for individual pitches. However, the strong influence of the pitch level (or content) would have such a crucial effect on the anode properties that it had to be taken into account.

Initial results obtained with commercial pitches from Koppers Denmark, Nyborg, had shown that the highest baked apparent density of the anodes was obtained by using 14 % pitch in the anode recipe for the petroleum pitch and 16 % pitch for the coal tar pitch. It was therefore decided to make anodes with a pitch level of 14, 15 and 16 % (w/w) from all the pitches. This allowed enough pitch in reserve to produce anodes with a pitching level of either 13 % (w/w) or 17 % (w/w), depending on the baked apparent densities obtained in the previous productions.

6.3.1. Mixing

In this process pitch and coke blend are mixed to yield a green mix of anode paste. In this context, “green” does *not* refer to the color, but is an industrial description used for

materials which are not fully carbonized. The mixing took place in a sigma blade mixer with two rotating blades. The mixer was preheated to approximately 190°C by a hot-oil system. The pre-weighted blend of coke was added to the heated mixer and the mixer blades were started. 2-3 kg of pitch were added to obtain the right pitching level. After 20 to 25 minutes the mix had reached a temperature of 170°C. The rule of thumb in mixing is that the final temperature should be 50°C above the softening point of the pitch. After 25 minutes or when the mix had reached a temperature of 170°C, the mixer was stopped and the green mix was ready.

6.3.2. Molding

In this process, the green mix was molded into green anode blocks. A specialized vibrating unit was used to form green anodes with a diameter of 10 cm and a height of 17-18.5 cm. The preheated mold (~155°C) was charged with 2.3 kg of green paste. The mold was situated on a vibratory table (see Figure 6-1) where two rotary electric motors provided a vertical motion based upon a motor frequency of 51 Hz with an amplitude of 0.635 cm. A plenum was used to apply a surface force to the anode equivalent to 0.85-1 bar. Each anode was vibrated for 65 seconds. Each green mix batch provided material for six anode blocks.

6.3.3. Baking

The baking system employed in this study consisted of an inconnel container placed inside an insulated box, and the heating system consisted of three zones of silicone carbide elements. The baking retort was purged with nitrogen through the baking cycle to avoid air burn of the anodes. The green anodes were evenly spread within the retort (max. thirty green anodes) and covered by finely divided coke. The container lid was placed on the container and sealed with alumina. The anodes were baked by application of the following baking profile:

0°-600°C: 10°C/hour

600°-1170°C: 25°C/hour

1170°C: 20 hours

Natural cool down to ambient

The actual internal maximum container temperature was between 1080°-1130°C in the final part of the bake cycle.

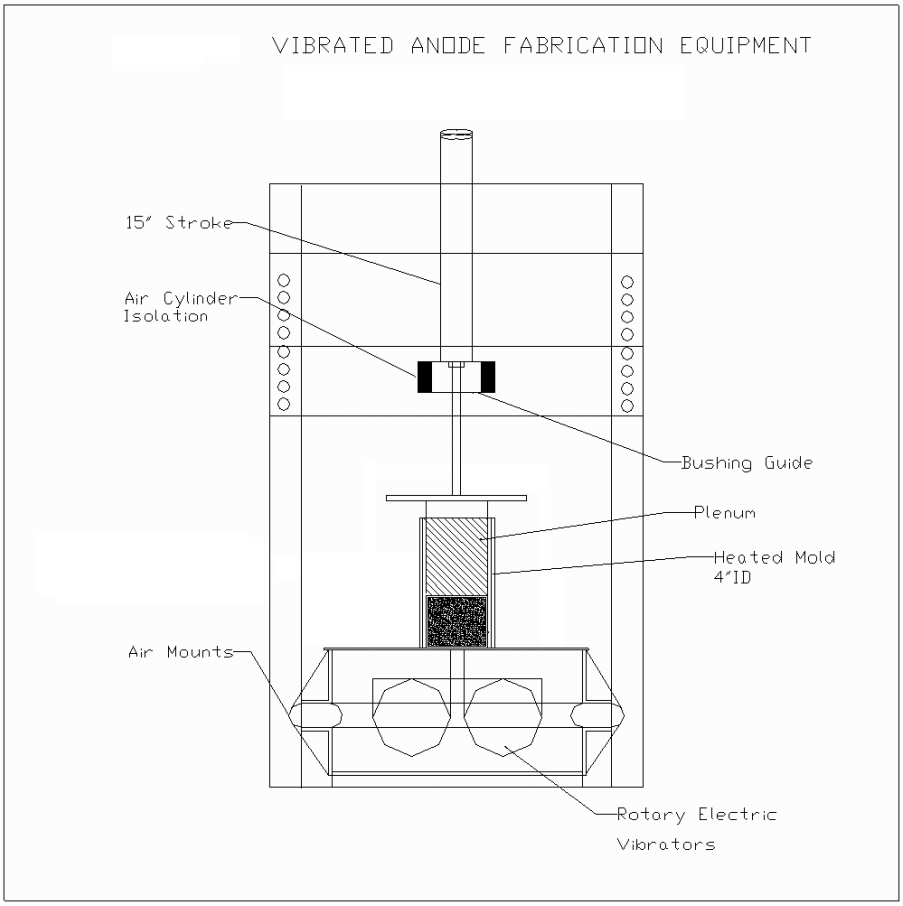


Figure 6-1: Schematic drawing of the mold at the vibrating table. (Figure used with the permission of the Harmarville Technical Center).

6.3.4. Core Drilling the Anodes for Test Pieces

Most anode tests require core samples. In order to prepare the anode for testing, a core of 50 mm diameter is drilled out of the center of the baked anode blocks. The ends are cut off

the block leaving a 130 mm long core. This process removes the surface layer of the anode and leaves a more homogeneous material.

6.3.5. Testing

The anodes were subjected to a comprehensive evaluation test scheme in order to find out whether the experiment binders influenced critically the anode quality. Figure 6-2 shows the carbon-testing program of Koppers Technical Center, Harmarville, as a schematic. The individual test methods are listed in Table 6-3 and a more throughout description is found in Appendix H. The anode-testing program consists of both destructive and non-destructive tests. The entire anode population was submitted to the non-destructive tests as baked apparent density (BAD) and electrical resistivity (ER). After the non-destructive tests, the anode group was split into two groups in order to be able to perform a series of more time consuming or destructive tests.

6.4. Results

The full carbon-testing program was applied because the influence of the thermal treatment and the different materials was not understood in advance. Several of the test parameters turned out not to be influenced by the binder or were found to be a function of binder content rather than the properties of the pitches themselves. The test values are listed in Appendix I and a selection of the data will be presented in the following section. The values are averages of three or six data points obtained for a particular pitch type at one pitching level.

6.4.1. Baked Apparent Density

Baked apparent density (BAD) is one of the most important quality measures of the anode. There are two reasons for this prominent position. First, it is rather informative and many of the anode properties which will be discussed in the section are correlated with the BAD. This means that once the BAD has been optimized, good overall anode properties generally follow. Secondly, the analysis is relatively simple and non-destructive, so that

the BAD can be routinely measured on all anode samples allowing them subsequently to be utilized for other tests. The value of the BAD should be as high as possible.

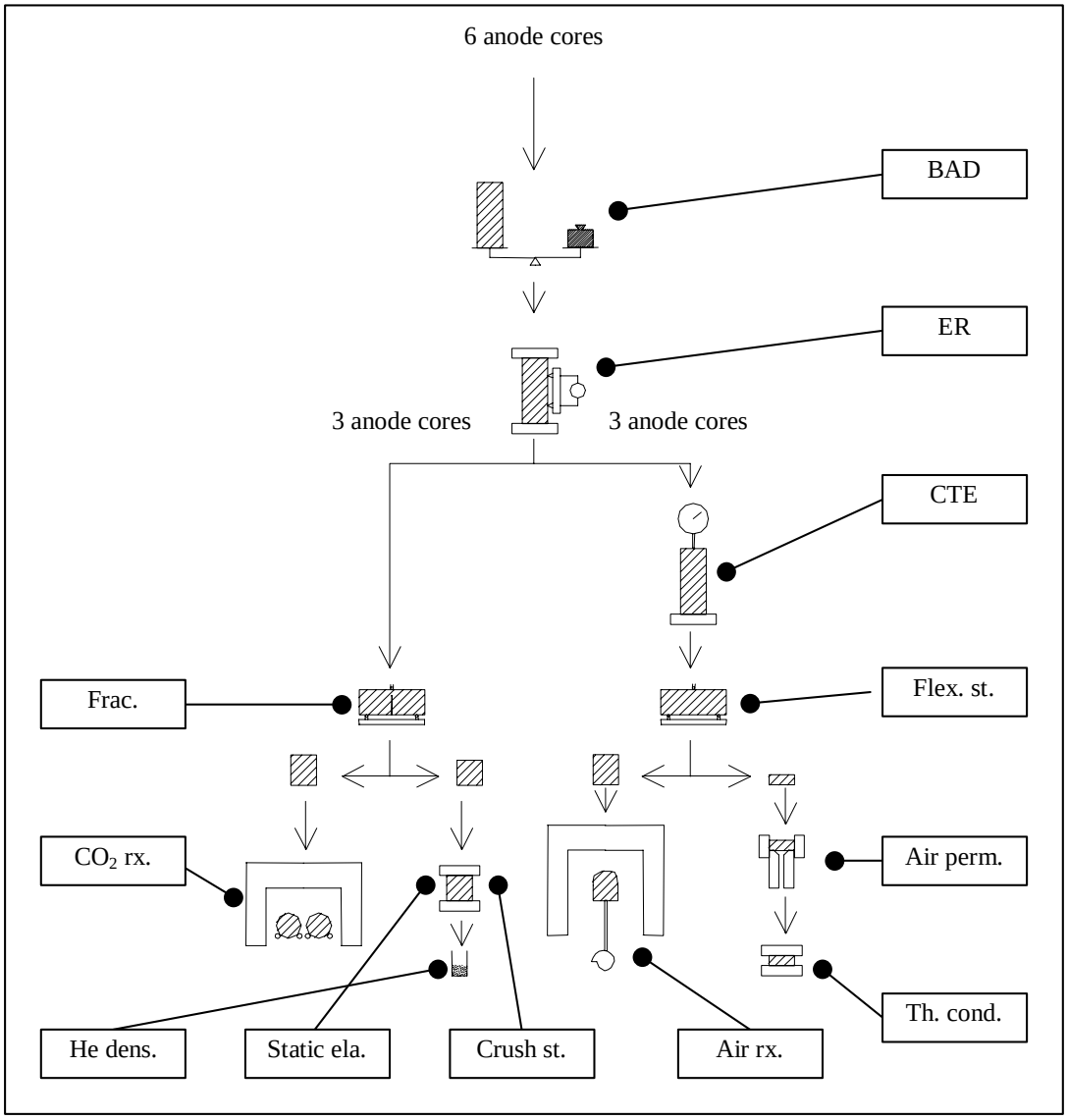


Figure 6-2: Carbon testing program for experimental anode recipes at Koppers Technical Center, Harmarville.

Figure 6-3 shows the BAD measured on the anode cores as a function of the pitching levels. The properties which have the most pronounced influence on the BAD are the pitch type and the pitching level. The petroleum pitches clearly show a much lower BAD than the other pitch types even at the optimum pitch level.

Name	Abbreviation	Unit	Test size
Green apparent density	GAD	kg/dm^3	6
Coking value of pitch in anode	in situ CV	%(w/w)	6
Shrinkage	Shrink.	%(w/w)	6
Baked apparent density	BAD	kg/dm^3	6
Electrical resistivity	ER	μΩm	6
Coefficient of thermal expansion	CTE	K	3
Flexural strength	Flex. st.	Pa	3
Compressive strength	Crush. st.	Pa	3
Static elasticity	Static ela.	Pa	3
Fracture energy	Frac.	J/m^2	3
Thermal conductivity	Th. cond.	W/mK	3
Air permeability	Air perm.	nPm	3
True density	He dens.	kg/dm^3	3
Air reactivity residue	Air rx. res.	%(w/w)	3
Air reactivity dust	Air rx. dust	%(w/w)	3
Air reactivity loss	Air rx. loss	%(w/w)	3
CO_2 reactivity residue	CO_2 rx. res.	%(w/w)	3
CO_2 reactivity dust	CO_2 rx. dust	%(w/w)	3
CO_2 reactivity loss	CO_2 rx. loss	%(w/w)	3

Table 6-3: Properties measured in the anode study. Test sizes refer to the number of pieces tested.

The mild thermal treatment of coal tar pitch during manufacture leads to a higher pitch requirement in order to obtain the same BAD (Figure 6-4), but the BAD obtained at the optimum pitch level was not improved. The petroleum pitch reacts much differently to the thermal treatment of the topped precursor tar than the coal tar material. Figure 6-5 shows that the pitch requirement is increased by the treatment but a pronounced increase is also observed in the BAD. Even though the thermal treatment increased the BAD, it is still far inferior to the results which were obtained by the coal tar pitch.

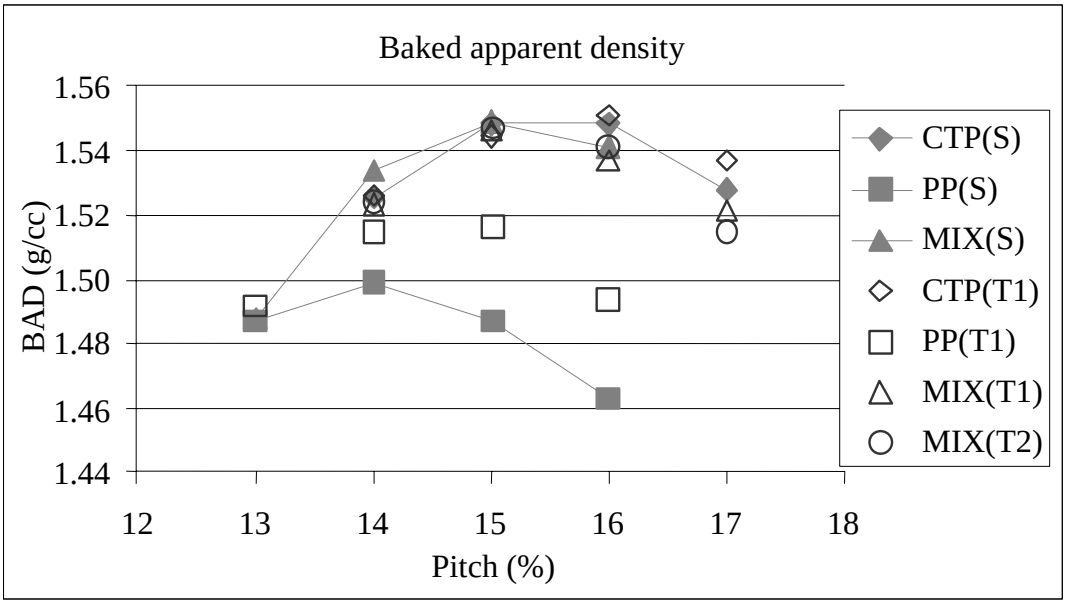


Figure 6-3: Baked apparent density measured on the core. Legend: pitch type (see Table 6-1).

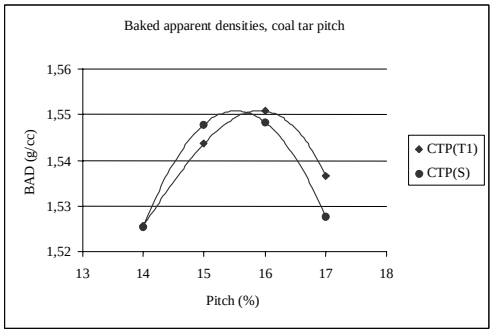


Figure 6-4: BAD of the coal tar pitches as functions of pitch levels.

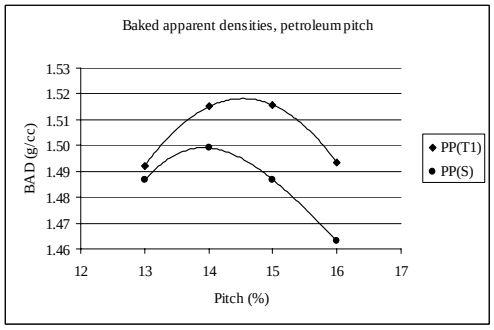


Figure 6-5: BAD of the petroleum pitches as functions of pitch levels.

Figure 6-6 and Figure 6-7 show the BAD of the straight distilled and of the pitches made from thermally treated materials. As noted before, the anodes which were obtained by use of petroleum material were inferior to the results obtained by the other pitches. The blended pitch was on the other hand performing remarkably well. The BAD at the optimum pitch level is comparable with the results obtained by coal tar pitch. At the same time, the pitch requirement at the optimum is reduced by half of a percent absolute.

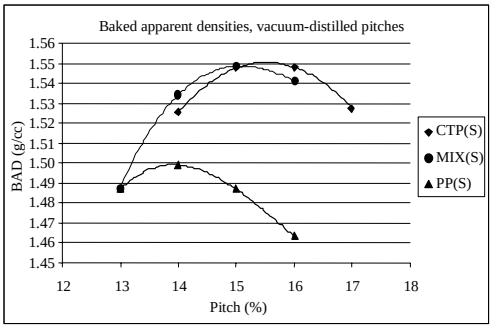


Figure 6-6: BAD of the straight distilled pitches as functions of pitch levels.

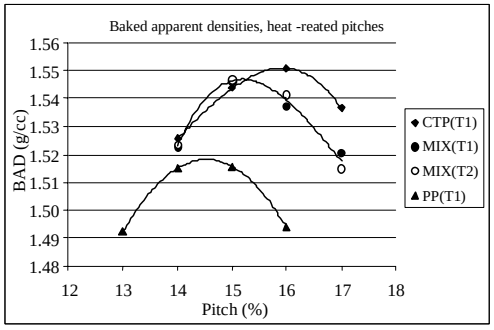


Figure 6-7: BAD of the pitches from thermally treated material as functions of pitch levels.

Based on the experiments which were described in Chapter 2 it was questioned whether there was any interaction between coal- and petroleum-derived materials during the thermal treatment. For further investigation of this question, two blended pitches were prepared including thermal treatment. MIX_{T1} was prepared as a simple mix between PP_{T1} and CTP_{T1} while MIX_{T2} was distilled from a thermally treated blend of topped tars. The two materials perform similarly and in Figure 6-7 they are fitted by the same third-degree polynomial. The anodes prepared from blends are better than they would have been from the parent pitches, especially in view of the poor performance of the petroleum pitch on its own. The positive interaction between the coal-derived material and the petroleum-derived material during anode preparation, which had been observed by Wombles et al., 2000, is further indicated by the present study.

The true density or rather the density of the combined pitch and petroleum coke (see Appendix H and I) is approximately the same for all the anodes. This means that the BAD shows a direct relationship with the air permeability and the porosity of the anode.

6.4.2. Electrical Resistivity

Figure 6-8 shows the electrical resistivity (ER) of the anodes as functions of pitch content in the anodes. Electrical resistivity is an important parameter in the utilization of the anodes and has an influence on the current efficiency which can be obtained by using the anodes in the energy intensive aluminum smelting process. The coal tar pitches and the blended pitches show the same tendency with respect to the pitch level. The ER is reduced

with increasing pitch level until 15%, after which it remains constant at 60 μΩm. The petroleum pitches generally exhibit a higher ER, meaning that the anode will consume more energy in actual use. It should be noted that the blended pitches perform comparably to the coal tar pitches and that these two materials are neither improved nor made worse by the thermal treatment.

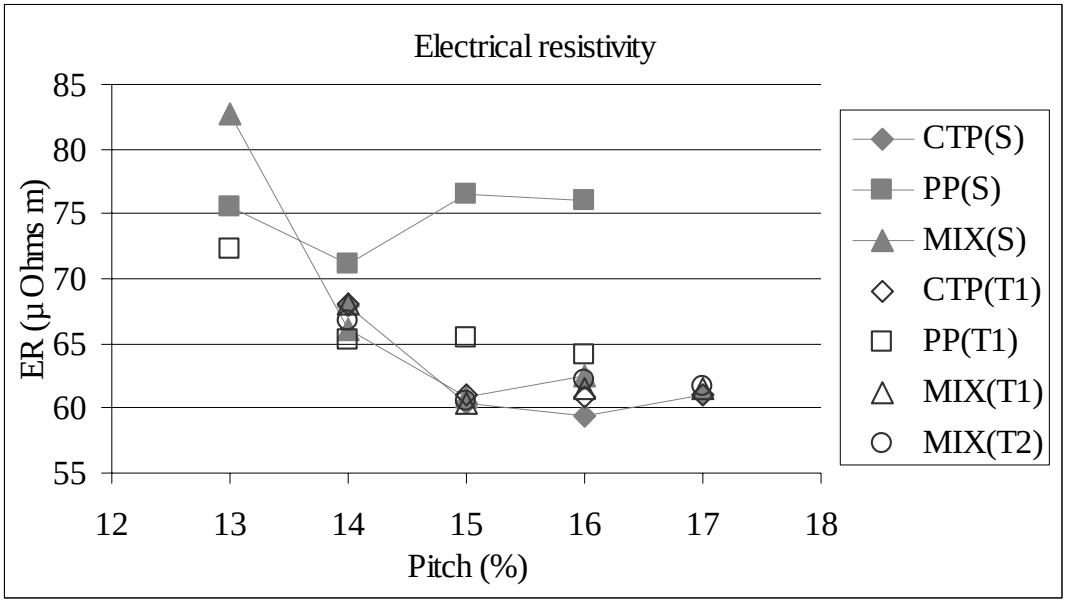


Figure 6-8: Electrical resistivity as a function of pitching level. Legend: pitch type (see Table 6-1).

6.4.3. Air Reactivity

The air reactivity of the anodes turned out to be strongly affected by the pitch type. Figure 6-9 shows the residue from the air reactivity measurement as a function of the pitch level with the pitch type as legend. The anodes which were produced from petroleum pitch give a reduced overall residue compared with the other pitch types. The fraction of the anode which actually reacts with the air and is lost as gas is relatively constant for all pitch types (Figure 6-10). Figure 6-11 shows that the amount of dust from the anode is sensitive to the binder pitch type. (The dust is produced during the experiment or removed by the ball mill, see Appendix H for further description of the analysis).

The higher air reactivity is probably caused by two mechanisms. First, the higher air permeability of the PP anodes gives the air access to a larger surface, which again promotes a higher reactivity of the anode. Another plausible explanation is that the coked binder matrix from the petroleum-derived pitch is more reactive causing a selective air burn of the binder matrix. The combined result of these two mechanisms is an increased amount of dust from the anode.

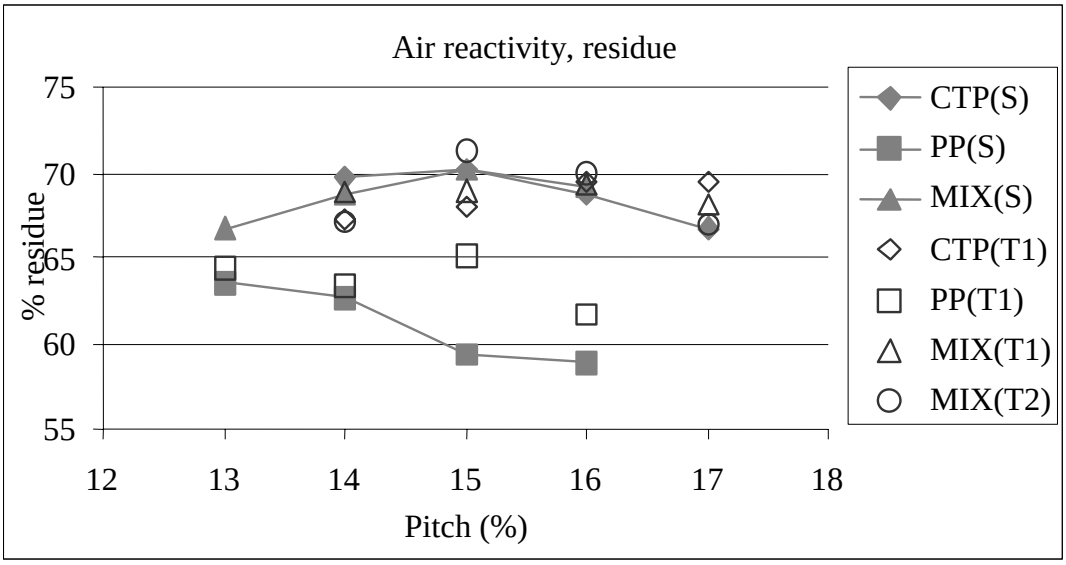


Figure 6-9: Air reactivity residue as a function of pitch level. Legend: pitch type (see Table 6-1).

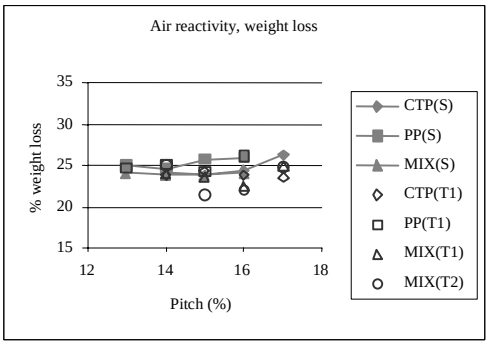


Figure 6-10: Air reactivity weight loss as a function of pitch level.

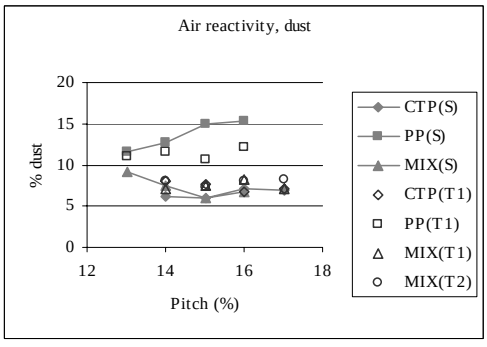


Figure 6-11: Air reactivity dust as a function of pitch level.

6.4.4. Analysis by Optical Microscope

Selected anodes were sent to Ralph Gray Service for a microscopic analysis similar to the analysis of some of the pitches which was described in Chapter 4. In the anodes it is the carbonized pitch which glues together the particles of aggregated coke. The aim of this analysis was to obtain information about the pitches by studying their carbonized form and to study how the carbonized pitch binder integrated with the petroleum coke to make a homogeneous anode.

The disks, measuring 20mm in height and 50mm in diameter, which had been used for air permeability and thermal conductivity were used for the analysis because this section was the last part of the anodes which remained in a physical sense after the test program. The sample was taken from the first anode which had been made from the anode mix. A pie-shaped sample, representing about a quarter of each disk was cut and mounted in epoxy in 1¼ inch cylindrical ring mounts. The mounted sample surfaces represented a section through the thickness of the disks from the edge to the center. Each baked anode sample was ground and polished for use in microscopic examination.

To aid the analysis of the carbonized pitch coke, anodes with maximum levels of pitch were chosen even though they would be slightly over-pitched. Unfortunately for the analysis, the pitch turned out to be very well mixed with the coke, so the fines were well integrated into the pitch coke. While the result was a better anode quality, it was impossible to distinguish the pitch coke from the petroleum coke. According to Ralph Gray, this was often observed in the case of low QI pitch.

Photographs of anodes produced from the pitches CTP_S, PP_S, CTP_{T1} and PP_{T1} are shown in Figures 6-12 to 6-23. The pictures have been taken in reflected light using magnifications of x80, x450 and x2000. Figures 6-16 to 6-23 have been taken in polarized light using a retarder plate to enhance the structures of the coke. In the pictures some of the recognizable structures are marked:

P: Coarse petroleum coke

F: Fine sized petroleum coke and pitch coke

V: Voids

Figures 6-12 to 6-15 show pictures of the anode surfaces at low magnifications. Based on the visual impression CTP_S has yielded a good anode structure. The pores are small and evenly distributed and the space between the coarser coke grains has been filled up with a fines/pitch coke mixture. The anodes which were produced by 16% PP_S yielded some of the worst anodes produced in this study according to the analytical results. This negative evaluation is underlined in Figure 6-13 where large voids are visible in the surface. During the baking process, the pitch developed large quantities of volatiles causing the anode block to expand. This led to a porous structure with interconnected voids. The T1 pitches (see Table 6-1) yielded anodes where the structure lies somewhere between that previously described. The structure of the anodes bound by coal tar pitch produced with thermal treatment is not as fine as for counterparts where the coal tar pitch was straight distilled. The structure of the petroleum pitch anode was much improved compared with the PP_S anode. Smaller voids were, however, still appearing.

Figures 6-16 to 6-19 show a comparison of the interaction between the coke particles and the fines/pitch coke matrix. The anodes made from the coal tar pitches have a structure where the space between the coarser grains is packed with intermediates and fines giving a compact anode matrix. In the anode made from PP_S the pitch seems almost to be drawn into the coke grains, leaving little to wet the coke surface. Fine cracks are often seen on the surface of the coke grains as if the pitch coke had not been able to bind properly to the petroleum coke. This surprising observation can be further studied in Figures 6-20 to 6-23 where pictures of how the pitch coke domains (F) interact with coke particles (P) are shown. In Figures 6-20 and 6-22 the pitch coke is observed to bind tightly to the grain surface. In Figures 6-21 and 6-23, where anodes made from petroleum pitches are shown, cracks have been formed between the two materials. Intuitively, it would be expected that coke from petroleum pitch would bind at least as well to petroleum coke as coke from coal tar pitch. The cracks must have been formed during the last carbonization processes where the petroleum coke has shrunk.

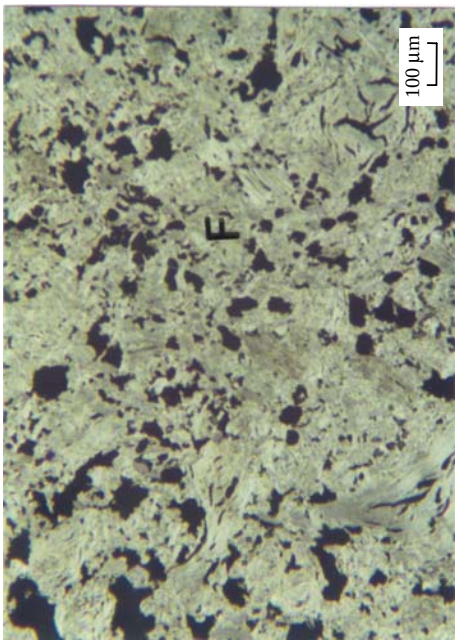


Figure 6-14: Anode produced with 17% CTP_{T1}, x80, reflected light.

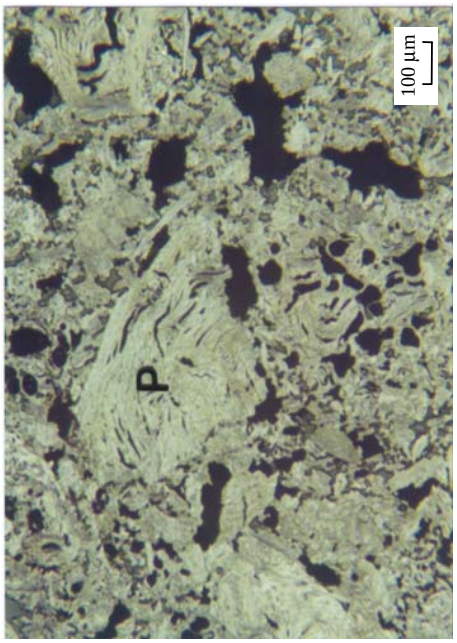


Figure 6-15: Anode produced with 16% PP_{T1}, x80, reflected light.

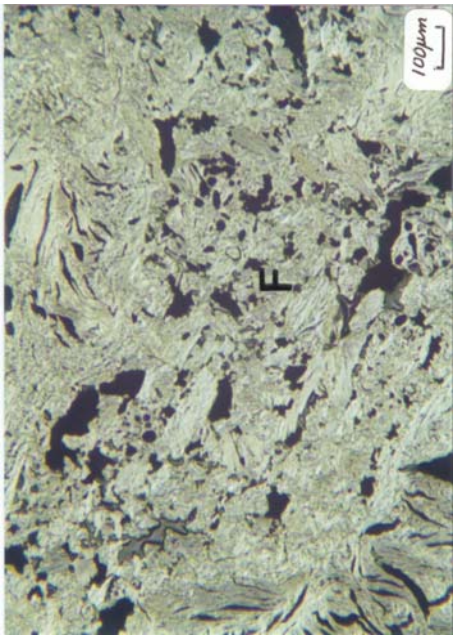


Figure 6-12: Anode produced with 17% CTP_S, x80, reflected light.

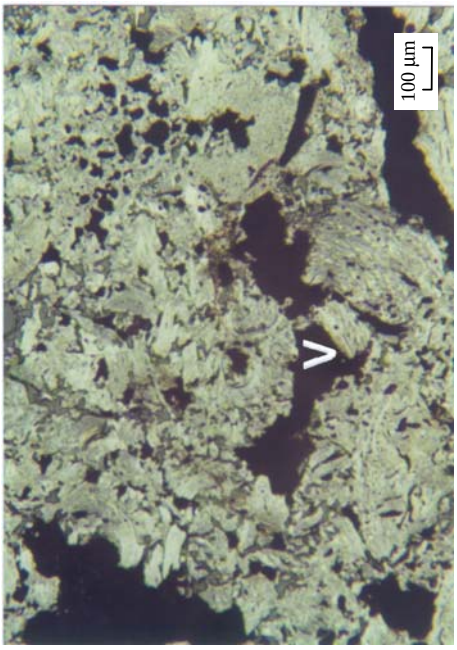


Figure 6-13: Anode produced with 16% PP_S, x80, reflected light.

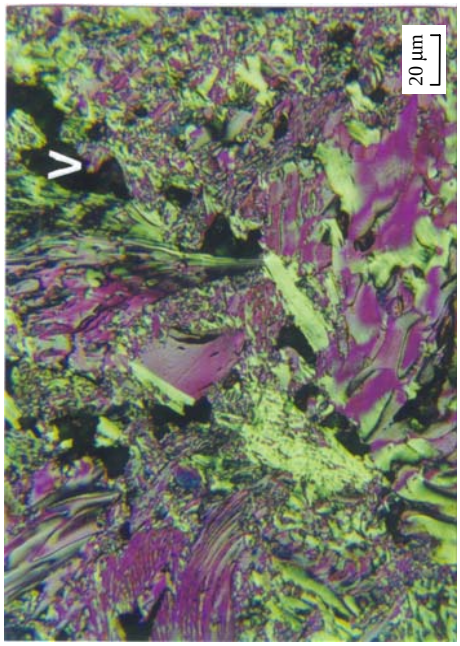


Figure 6-16: Anode produced with 17% CTP_S, x450, reflected polarized light in oil.

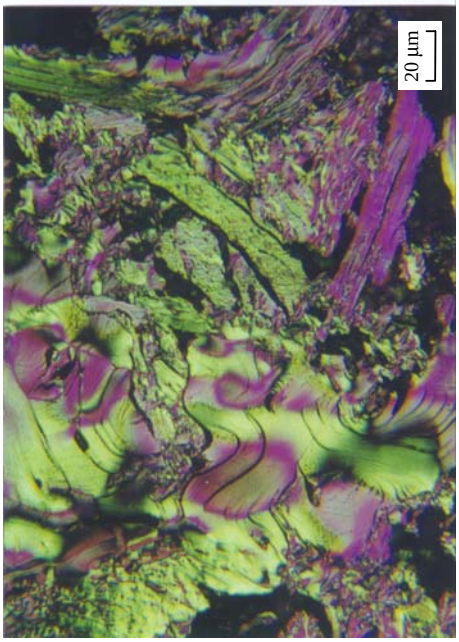


Figure 6-17: Anode produced with 16% PP_S, x450, reflected polarized light in oil.

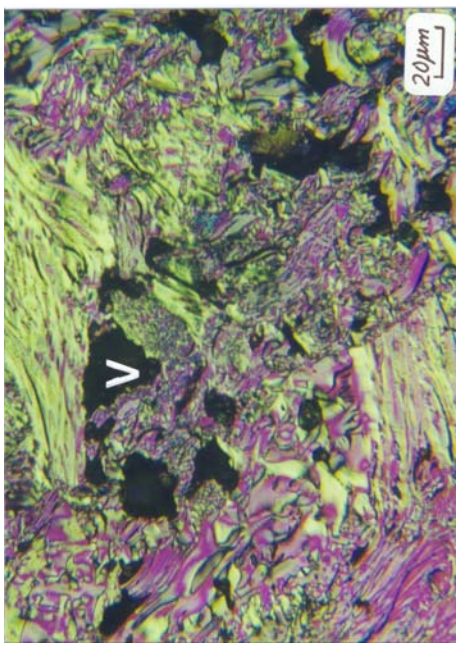


Figure 6-18: Anode produced with 17% CTP_{T1}, x450, reflected polarized light in oil.

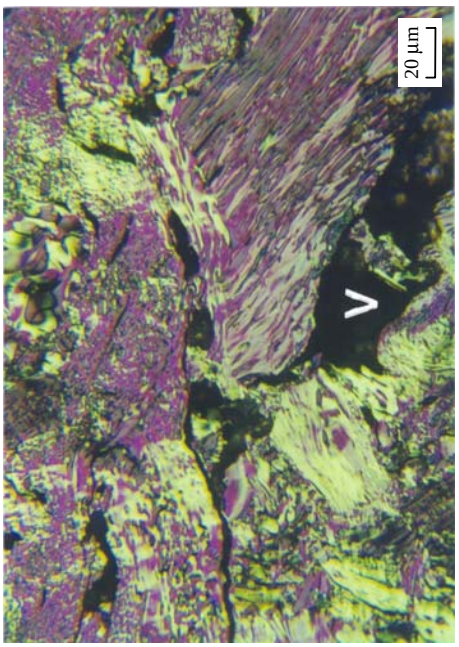


Figure 6-19: Anode produced with 16% PP_{T1}, x450, reflected polarized light in oil.

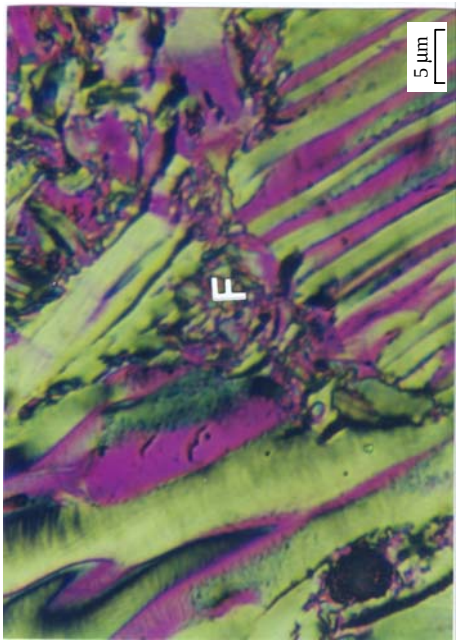


Figure 6-22: Anode produced with 17% CTP_{T1}, x2000, reflected polarized light in oil.

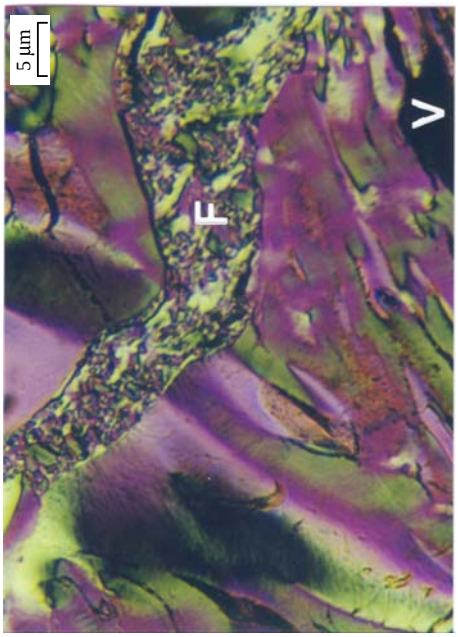


Figure 6-23: Anode produced with 16% PP_{T1}, x2000, reflected polarized light in oil.

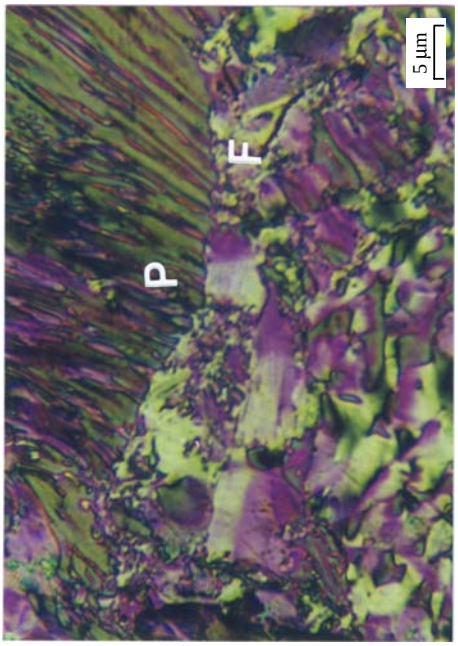


Figure 6-20: Anode produced with 17% CTP_S, x2000, reflected polarized light in oil.

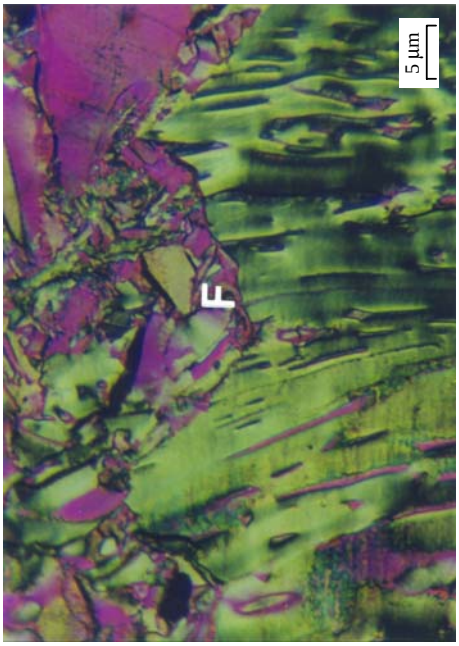


Figure 6-21: Anode produced with 16% PP_S, x2000, reflected polarized light in oil.

An anode made with 17% of the blended pitch MIX_{T1} was also submitted to analysis. Unfortunately, this particular anode slice contained an unexpected amount of sponge coke and the structure of the anode was extremely poor. This result was not expected so one of the anodes produced with 16% MIX_{T1} was additionally analyzed. The anode had a structure similar to CTP_{T1} and PP_{T1} with a tendency to cracks at the surface of the coarse coke grains, which had also been observed for the petroleum pitch anodes. This result was more in line with the other analysis and probably represented the true picture. The example underlines the weakness of this limited microscopic analysis, where a large quantity of material has been reduced to analysis of an area of five cm^2.

6.5. Analysis and Discussion of Results

6.5.1. Anode Properties

In the anode study, a large array of anode properties has been measured. In order to be able to discuss these results, a source of the typical range of the properties for commercially manufactured anodes has been found. Meier, 2000, listed typical ranges of most of the properties which were measured in this study. The values are listed in Table 6-4 together with the values obtained in this work. In a comparison of the values it should be noted that properties of the test anodes are often outside of the typical range and inferior. The anodes which were produced from the petroleum pitches have generally difficulties in meeting the expectation range for the industrially produced anodes. Especially, the straight distilled petroleum pitch PP_S has yielded a poor anode quality.

By use of the optimum pitch levels, the anodes from the CTP and MIX series meet the majority of the specifications. The test anodes generally show a lower strength (both flexural and compressive) and fracture energy. These types of differences can often be observed between lab-scale and industrially produced anodes. The larger quantities used in industry allow further optimization of the anode materials and production the conditions. If the effect, however, were genuine, it might influence the tendency of the anode to break during handling or because of the thermal shock (TS) the anodes experience when lowered down in the electrolytic bath. The TS will be analyzed in Section 6.5.2.

Properties		Units	Typical range	Range, this study	Comments
Baked apparent density		kg/dm^3	1.54-1.60	1.46-1.55	CTP + MIX anodes are ok in optimum conditions
Spec. electr. resistivity		$\mu\Omega m$	50-60	59-83	CTP + MIX anodes are ok in optimum conditions
Flexural strength		MPa	8-14	2-8	All samples are low. Linear function of pitch level
Compressive strength		MPa	40-55	20-44	CTP_S is ok in optimum conditions
Elasticity modulus	static	GPa	3.5-5.5	0.9-3.1	All are low, advantage by thermal shock sensitivity
Coeff. therm. expansion	20°-300°C	$10^{-6}K$	3.5-4.5	3.6-3.8	All are ok and in the low end, advantage by thermal shock sensitivity
Fracture energy		J/m^2	200-300	44-258	All samples are low. Linear function of pitch level
Thermal conductivity		W/mK	3.0-4.5	1.7-2.6	All are low, disadvantage by thermal shock sensitivity
Density in xylene		kg/dm^3	2.05-2.10	2.04-2.07[a]	Unaffected by pitch type and level
Air permeability		nPm	0.5-2.0	0.4-4.5	CTP + MIX anodes better than typical range in optimum conditions
CO_2 reactivity	residue	%	84-95	80-88	CTP + MIX anodes are ok in optimum conditions
	dust	%	1-10	3-8	All anodes are ok
	loss	%	4-10	9-13	CTP + MIX anodes are ok in optimum conditions
Air reactivity	residue	%	65-90	59-71	CTP + MIX anodes are ok in optimum conditions
	dust	%	2-10	5-16	CTP + MIX anodes are ok in optimum conditions
	loss	%	8-30	21-26	All anodes are ok

[a] Measured in helium

Table 6-4: Anode properties of the anode study. Typical range as reported by Meier, 2000, compared to the range of this study.

6.5.2. Thermal Shock

The test anodes were found to have a relatively lower strength than the typical range of industrially produced anodes. This might lead to unfortunate results in real use. When a new, cold anode is lowered into the hot cryolite, electrolytic bath it experiences a thermal shock. Depending on the local temperature distribution, this causes thermal expansion of the material. Local differences in the thermal expansion of the anode result in thermal stresses and can further lead to cracking of the anode. This phenomenon is known as thermal shock (TS). Thermally cracked anodes are the cause of severe cell disturbance when pieces of carbon fall into the pot.

Meier et al., 1994, presented a model for prediction of the thermal shock resistance (TSR) of an anode. The model was derived from theories valid for brittle solids placed under stress and crack propagation. Other authors have worked at discovering the factors influencing the TSR of anodes, but the work of Meier distinguishes itself by allowing calculation of a global index which indicates the resistance of a present anode material without prior knowledge of the previous line of anodes during pot operation. The TSR can be calculated from Equation 6-1.

$$TSR = \sqrt{\frac{2G\left(\frac{V_{sample}}{V_{anode}}\right)^{\frac{1}{m}}}{\pi a E}} \frac{2\lambda(1-\nu)}{\alpha L h Y \Delta T} \qquad \text{Equation 6-1}$$

TSR	[-]	thermal shock resistance
G	[J/m^2]	fracture energy
V_{sample}	[m^3]	stressed volume of sample core during fracture energy measurement
V_{anode}	[m^3]	stressed volume of the full size anode
m	[-]	Weibull´s modulus
π	[-]	the number phi
a	[m]	characteristic crack dimension
E	[N/m^2]	static modulus of elasticity
λ	[W/mK]	thermal conductivity
ν	[-]	Poisson´s ratio
α	[K^{-1}]	coefficient of thermal expansion
L	[m]	characteristic length of the anode
h	[W/m^{2}K]	conductive heat transfer coefficient
Y	[-]	dimensionless function depending on the geometry and loading
ΔT	[K]	initial temperature difference between bath and anode

The practical significance of the TSR is the following:

TSR > 1 no anode thermal shock failure is expected

TSR < 1 anode thermal shock failure is expected

The parameters which are included in the TSR model are influenced by anode raw materials, anode manufacturing process and electrolytic cell conditions. The parameters influenced by raw materials are α, E, G, a, ν and λ according to Meier et al., 1994. In the following calculation the parameters which are not influenced by raw materials are taken directly from the typical case used by Meier et al., 1994, and it is thus assumed that the anodes have similar dimensions and are used in a similar fashion. Of the six parameters influenced by raw materials α, E, G and λ were measured during this study. Poisson´s ratio (ν) indicates lateral strain relative to a direct tensile strain (Van Vlack, 1989). No other sources were found concerning the magnitude of this parameter in carbon materials so the value of Meier et al., 1994, was used. Likewise, the characteristic crack dimension (a) was adopted directly from this work.

Apart from being a result of the parameters the TSR is also a statistical problem. The anode properties are distributed around a mean value and only the weakest anodes will crack. For a statistically sound investigation, hundred samples are required while thirty are mentioned as the absolute minimum (Meier, 2000). In the present work, six anodes were produced for each formulation. The most correct approach would have been to calculate the TSR for every anode. This was complicated by the fact that E and G for practical reasons were measured on other anode cores than α and λ (Figure 6-2). Thus, the average values were used and together with the low population, this might give unrealistic values of TSR. The method was anyway applied in order to test the significance of some of the measured properties.

Figure 6-24 shows the TSR as a function of pitch level for the different pitch types. The figure reveals that the TSR of the materials is more favorable than expected from the lower strength found for the anodes. The low values of fracture energy (G) and thermal conductivity (λ) are counterbalanced by equally low values of coefficient of thermal

expansion (α) and modulus of elasticity (E). Lab-scale anodes produced with very low binder pitch content are not performing well, but anodes produced with optimum pitch level from CTP or MIX pitches would probably not lead to thermal shock problems on the basis of the calculations.

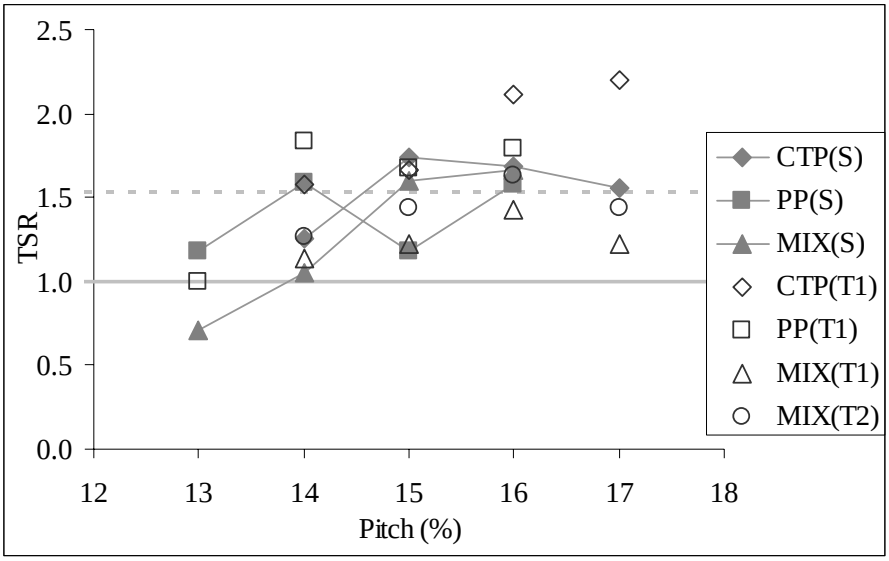


Figure 6-24: Thermal shock resistance (TSR) of the test anodes as a function of pitch levels. The critical TSR (1.0) and the typical TSR (1.53) are given as horizontal lines. Legend: pitch type (see Table 6-1).

6.5.3. Influence of Pitch Type

In Chapter 2, it was investigated how pitch properties could be influenced by thermal treatment of topped tar. It was found that the treatment was capable of increasing coking value (CV) and toluene insoluble (TI) without influencing the quinoline insoluble (QI). The mentioned analytical properties are normally used in routine quality assessment of binder pitches in Koppers Denmark as well as in the aluminum industry. The present study has applied pitches with different characteristics and based on this data it will be attempted to get an idea about how the anode properties are influenced by the properties of the binder pitch. It should be noted that due to the limited number of materials in this study the findings might not be general and they should not be directly transferred to other materials.

The correlation between the analytical properties of the pitch (Table 6-2) and the anode properties (Appendix I) was calculated. Some of the properties were highly influenced by whether the optimum amount of pitch was used for the anodes. To assure that the pitch types were treated equally the data set of the anodes which gave the highest BAD measured on the anode core was chosen for the correlation analysis. The results of the calculation are listed in Appendix J and an interpretation will be given in the following section.

The QI, ash content and density of the pitch were correlated with the amount of coal tar material in the pitch. The correlation between these parameters was so strong that it was not possible to separate individual effects. In the microscopic analysis of the pitches produced from thermally treated materials some small mesophase spheres were found but this content did not cause a large increase in the QI of these pitches. BAD, in situ coking value and residue of air and CO_2 reactivity measurement were increased with increasing amounts of coal derived material. At the same time ER, air permeability and dust from air and CO_2 reactivity were decreased. The results were governed by the fact that the petroleum pitches had performed poorly and that these pitches did not contain any QI.

The CV (coking value) was to some degree correlated with the amount of coal-derived material in the pitch. The CV had the same positive influence on the anode properties and additionally it was found to influence positively the flexural strength and the thermal conductivity. The softening point (SP) was kept constant during the experiments and the analysis therefore shows that it has no significant effect, due to the limited data range.

TI was found to have a good influence on many of the measured anode parameters. This can, however, to a large degree be explained by the correlation of TI with QI and CV. The amount of β-resins (β-resin =TI-QI) is not strongly correlated with any of the analytical parameters measured on the anodes, and the correlation which was found can mainly be explained by the correlation of the β-resins with the CV (i.e. the correlation between the β-resins and the anode property X can be estimated by $\rho_{\beta, X} \approx \rho_{\beta, CV} * \rho_{CV, X}$). The TI or β-resins are important properties of pitch and they are routinely measured on binder pitch (e.g. Meier, 2000, Wombles et al., 2000, or Malmros et al., 2000). While the influence of

different kinds of QI is well understood the actual significance of the β-resins is largely unknown. The β-resins have been reported to decrease electrical resistivity and increase the flexural strengths of graphite electrodes (Wagner et al., 1988). The coking value was, however, not included in the calculation so this might partly explain the found relationship. In the present investigation the β-resins were found to have no significant influence on the anode properties. Similar conclusions were drawn by McHenry et al., 1994.

The effect of thermal treatment on the petroleum material is relatively easy to establish but it is more difficult to isolate for the coal-derived and blended pitches. The in situ coking value of the pitch in the anodes has been calculated by assuming that the coke blend was unaffected by the baking process, meaning that the entire weight loss of the anode during baking could be attributed to the pitch. Figure 6-25 shows the in situ CV as a function of the CV which was measured on the pitch by the ISO 6998 method. The figure illustrates the difference between the routes of manufacture. Both the straight distilled pitches and the pitches distilled from thermally treated topped tar show a linear relationship between the two types of CV. The general level of in situ CV is, however, lowered by the thermal treatment. Thus, the in situ CV of the coal-derived pitch is lowered by the thermal treatment even though the CV of the pitch (by ISO 6998) is increased. The in situ coking value of the blends are of the same magnitude regardless of the treatment while the coking value of the petroleum pitch is increased enough for the in situ coking value to increase as well.

There seems to be a systematic difference in the in situ coking value of the pitches produced by thermal treatments compared to the straight distilled pitches. This could indicate that the conditions under which the anodes were manufactured favored the straight distilled pitches, which is the commonest way of producing commercial binder pitches. There is a poibility that if the coke blends and anode manufacture conditions had been optimized for the individual pitch, better results could have been obtained for the pitches which were produced from thermally treated topped tar. Based on the results thermal treatment can, however, not be recommended for coal-derived material. Petroleum-derived material on its own does not seem to yield a good binder pitch. If petroleum pitch should

be used as binder pitch it seems reasonable to use some kind of careful thermal treatment during the manufacture.

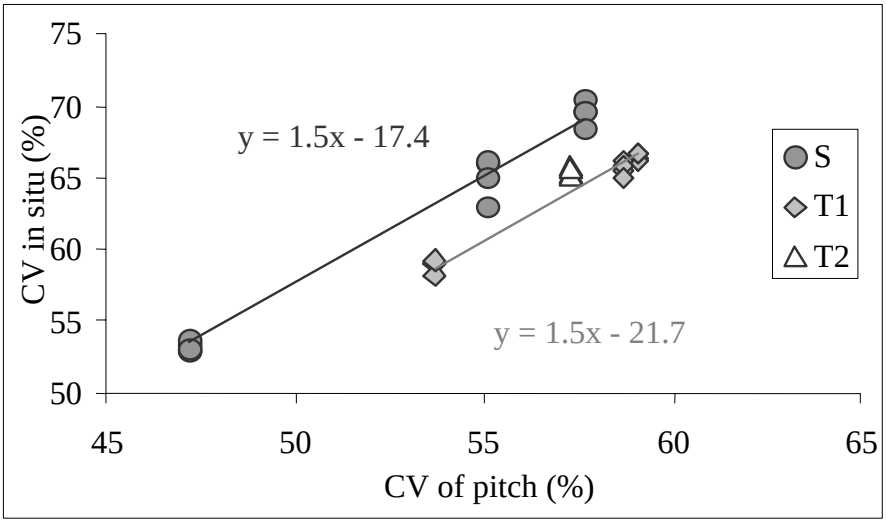


Figure 6-25: In situ coking values as functions of coking value measured on pitch. Legend: treatment, see Section 6.2.1 and Table 6-1.

6.6. Conclusion on the Anode Study

The best anodes were produced using the straight distilled coal tar pitch. Generally, all anodes which were produced using optimum pitch levels of the coal-derived pitches or the combined feedstock pitches gave good and comparable quality. The addition of 20 %(w/w) petroleum-derived material reduced the pitch requirements by half a percent. The thermal treatment had no large effect on the quality of these materials and based on the present results the treatment cannot be recommended as a sure and certain route to improvement of the anode quality.

The petroleum pitches had an inferior anode performance compared with the other materials. Some improvement was introduced by the thermal treatment but the quality never reached the one of the coal tar pitch. The pitch demand is smaller when petroleum pitch is used. If petroleum pitch should be used as binder, some kind of controlled thermal treatment can be recommended during the production.

The significance of the analytical properties of pitch has been examined. The fact that QI originated from coal tar made it impossible to judge this factor. The results indicate that the CV had additional positive effect on the anode properties. The effect of TI can be explained by the correlation of this property with QI and CV. Because of the limited size of the study, it is not possible to draw conclusions on the influence of softening point, quinoline insoluble, ash or density.

7. Conclusion

The main goal of this project has been to find out whether it is possible to improve the binder properties of pitch by subjecting the feedstock to a mild thermal treatment. The study has included manufacture of a large array of experimental pitch types. Pitches have been analyzed by conventional methods as well as some of a more scientific nature. Additionally, a study of bench-scale aluminum smelting anodes has been conducted in order to try to evaluate the pitches in a process which resembles the actual use of the product.

It is possible to alter the analytical properties of pitch obtained from a coal tar or a petroleum material and thus make it more attractive as binder material. Experiments showed that the best results were obtained by removing part of the low boiling components in the tar by distillation before treating it at 385°C for six hours. Following this treatment the material could be distilled into a 120°C softening point pitch with an improved coking value and TI, compared to the pitch obtained by direct distillation of the same tar. The material which was subjected to this treatment showed limited amounts of secondary QI or mesophase.

Petroleum material had the largest potential for thermal-treatment-induced enhancement. Analytical properties, as well as the properties of bench-scale anodes manufactured from the materials, were improved by thermal treatment of the precursor material. The quality of the petroleum pitch, however, never reached the well-proven quality of a directly distilled coal tar pitch.

The coal tar material showed some improvements as a result of mild thermal treatment of the precursor material. It was, however, found that the properties of bench-scale anodes made from the material were not improved when compared to pitch produced by straight distillation. The intensive thermal impact experienced by the tar in the coke ovens had probably reduced the capability of further heat-introduced improvements of this material.

Productions of pitches from combined coal tar and petroleum material showed that there was no significant difference whether the two materials were treated together or separately. It was not possible to detect any significant interaction between material from coal tar and material from petroleum tar in the temperature range which was applied (350°-410°C). The results indicate that pitches produced with 20% material of petroleum origin performed better in bench-scale anodes than it would have been expected from the performance of pitches produced from the pure parent materials. Apparently, positive interaction takes place in connection with actual carbonization of the pitch.

The treatments of the pitch used for bench-scale anodes were designed to give a maximum increase in TI and CV without resulting in mesophase formation. Based on a study of the pitch by optical microscope the pitches, however, bore early indications of the thermal processes, meaning that the treatment was right on the edge of leading to actual mesophase formation. It was additionally found that the isotropic phase of the petroleum pitches was not completely homogeneous. The petroleum pitches contained areas with reduced viscosity where polishing agents could get caught under certain circumstances. It was possible to remove these domains by addition of coal tar pitch. The exact influence of the domains is not known, but if they remain stable in the pitch at higher temperatures they might to some extent be linked with the poor performance of petroleum pitch as binder.

Thermal treatment of the petroleum product leads to loss of aliphatic side chains. Several lighter components which could be analyzed by GC acted as hydrogen acceptors, indicating that polymerization and cyclization took place between large aromatic molecules.

It was possible to analyze the NMP soluble part of the TI fraction by size exclusion chromatography. These classes of components are normally difficult to analyze due to their low volatility and low solubility in most solvents. The analysis showed that heavy or rather early eluted components appeared in the petroleum pitch as a result of thermal treatment of the precursor material. Based on the results these components seem to be involved in the mesophase formation. Addition of coal tar material strongly reduced the appearance of the

material eluted in this range, which could indicate the initiation of coal tar and petroleum material interaction.

It cannot be recommended to introduce the experiment production method, with thermal treatment of the topped tar for coal tar pitch. The straight distilled coal tar pitch was the material which performed best as a binder pitch in the bench-scale anode study and it will be difficult to improve further the already strongly heat-modified product without initiating some of the processes which should take place within the binder matrix. If a pure petroleum pitch product is considered as binder pitch, it seems reasonable to introduce some kind of thermal treatment as a part of the production scheme. Additionally, binder pitches produced from combined coal tar and petroleum material perform better in bench-scale anodes than expected from the performance of their parent materials. This study has underlined that even though empirical pitch analysis methods are capable of providing some information about the material they should be treated with caution, especially when used on new products.

7.1. Future work recommendations

A continuation of the project could include a larger array of feedstocks. It was found that thermal treatments led to the largest improvements on petroleum material, while the coal tar material was not significantly improved. Other potential binder pitch precursors could be studied. Additionally, it might be considered to experiment with blends of petroleum materials which had undergone some thermal treatment and straight distilled coal tar pitch.

If additional thermal treatment studies are initiated it should be considered to construct a new reactor. A design which would allow analysis of the formed gas as well as higher temperature would be recommendable.

In the study an inhomogeneity in the isotropic phase of the petroleum pitches was found. No literature was found on the subject but the phenomenon was reported to have occurred in some other petroleum pitch materials as well. It might be possible to obtain trace samples of the material for further analysis.

Finally, it may be considered to initiate a collaboration with other research groups which possess expertise in further analysis of pitch. Further understanding could possibly be obtained if experts in for instance solid state NMR carry out an analysis of samples from this study or from future studies.

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Appendix A: Description of Pitch Analysis

A.1. Softening Point (SP)

The softening point of a pitch was found by use of the ASTM D 3104 standard. Since pitch is a glass-like substance it has no distinct melting point which marks the transfer from solid to liquid. Instead an isoviscous temperature was measured. The softening point measuring method used in this study is the "Mettler softening point". It is defined as the point where the pitch has a viscosity of $2*10^4$ poises. A carefully specified ring was filled with pitch and placed in a Mettler FP 80 oven set 20°C below the expected softening point of the pitch. The temperature was increased by 2 °C/min until the softening point where the pitch flows out through the ring and breaks a light beam.

A.2 Toluene Insoluble (TI)

The toluene insoluble fraction (TI) was analyzed by the method ISO 6376. One gram of pitch was refluxed with 100 ml of toluene for thirty minutes in a 250 ml conical flask. The solution with the insoluble particles was transferred to a glass filter crucible (pore size: 10-16 μm) and filtered under suction. The filter cake was washed with 80°C toluene and finally with 10 ml of acetone. The filter was dried for at least one hour at 105°-110°C before weighing. TI is defined as the insoluble fraction given in weight percent under the empirical conditions of the test.

A.3 Quinoline Insoluble (QI)

The quinoline insoluble (QI) analysis was carried out using the ASTM D 4746 method. 4 ml of quinoline at 80°C was added to 1.6 grams of pitch in a 50 ml beaker and kept at 80°C for twenty minutes. It was transferred to a porcelain filter crucible of a pore size of 7 μm and filtered under suction. The filter cake was first washed with 80°C quinoline and then with 10

ml of acetone to remove the quinoline. The filter was dried for at least one hour at 105°-110°C before weighing. The result is given as the insoluble fraction in weight percent.

A.4 Coking Value (CV)

Coking value is measured by the ISO 6998 method. One gram of pitch was weighed into a porcelain crucible with a close-fitting, non-sealing lid. The porcelain crucible was located inside a larger nickel crucible, which was filled with coke in order to produce an inert atmosphere. The entire system was placed in a 550°C oven for 2.5 hours. The residual weight is expressed in weight percentage of the original sample.

Appendix B: Analytical Data of Pitches

In this appendix analytical data for experimentally produced pitches is presented. The pitches were given codes after the precursor material and the order of which they were produced. The following series were made:

K* Pitch produced from the petroleum tar F98015
TP* Pitch produced from the topped petroleum tar F98020
TC* Pitch produced from the topped coal tar F98017A
TM* Pitch produced from blends of the topped petroleum tar F98020 and the topped coal tar F98017A

The data is presented in tables which are built up according to the following structure:

Table entry	**Unit**	**Explanation**
Pitch	-	Pitch code
Treatment		
Duration	hours	Duration of thermal treatment
Temperature	°C	Temperature of thermal treatment
Yield		
After topping	% (w/w)	Total yield after the topping
After treatment	% (w/w)	Total yield after the thermal treatment
Pitch yield	% (w/w)	Total yield of pitch
Analytical		
SP	°C	Softening point
QI	% (w/w)	Quinoline insoluble
TI	% (w/w)	Toluene insoluble
CV	% (w/w)	Coking value

Pitch	K3	K15	K1	K10	K16	K14	K5	K11
Treatment								
Duration	6	6	6	6	6	6	6	6
Temperature	307	307	312	330	330	346	349	363
Yield								
After topping	90.2	79.5	90.2	90.2	79.5	79.5	89.6	89.6
After treatment	88.1	78.5	88.6	86.4	73.2	72.2	78.1	79.4
Pitch yield	60.6	58.7	56.7	60.3	58.6	56.7	55.9	57.2
Analytical								
SP	121.7	126.2	120.4	117.2	117.9	118.3	127.8	120.4
QI	0.1	0.3	0.4	0.5	0.5	0.2	0.1	0.2
TI	9.1	9.2	10.6	11.9	11.3	14.6	14.4	16.5
CV	47.2	48.0	47.9	47.8	47.6	50. 8	52.7	51.7

Pitch	K12	K13	K6	K8	K7	K9	K17	K18
Treatment								
Duration	6	6	6	6	6	6	6	6
Temperature	365	369	370	370	390	390	392	415
Yield								
After topping	89.6	79.5	89.6	90.2	89.6	90.2	79.5	79.5
After treatment	68.1	68.6	69.5	71.5	59.6	68.4	67.0	58.0
Pitch yield	56.9	56.8	58.3	56.4	58.6	57.9	59.2	56.4
Analytical								
SP	121.3	118.2	115.6	122.7	113.4	125.1	116.5	138.8
QI	0.2	0.3	0.1	0.3	1.8	1.7	1.9	9.3
TI	17.0	19.0	17.9	18.5	26.0	25.1	25.8	38.6
CV	52.2	52.6	52.1	53.2	54.3	56.0	53.8	61.1

Pitch	K20	K29	K27	K21	K30	K23	K24	K25	K26
Treatment									
Duration	0	0.5	1	2	4	6	8	12	16
Temperature	-	360	360	360	360	360	360	360	360
Yield									
After topping	79.2	79.2	78.4	78.4	79.2	78.4	78.4	78.4	78.4
After treatment	79.2	78.4	77.6	76.4	76.4	74.7	74.7	70.4	71.3
Pitch yield	62.2	64.8	61.8	57.7	62.7	57.8	56.7	58.5	59.3
Analytical									
SP	118.9	103.1	113.3	117.4	100.6	116.3	120.7	114.5	116.5
QI	0.1	0.4	0.0	0.3	0.2	0.3	0.2	0.0	0.0
TI	5.9	9.0	9.0	13.9	13.9	16.0	17.3	17.4	18.4
CV	44.2	43.7	45.3	51.5	47.0	50.7	52.2	51.0	51.6

Pitch	TP1	TP3	TP4	TP5	TM4	TM7	TM1	TM3
Treatment								
% topped coal tar	0	0	0	0	50.1	50.1	50.1	50.1
Duration	6	6	6	6	6	6	6	6
Temperature	350	370	385	410	350	370	385	410
Yield								
After topping	85.8	85.8	85.8	85.8	82.9	82.9	82.9	82.9
After treatment	83.1	81.0	73.1	66.5	80.0	77.2	77.7	69.9
Pitch yield	55.1	56.3	55.9	55.9	55.3	52.5	55.4	57.8
Analytical								
SP	120.1	113.7	115.4	128.9	116.2	120.9	127.9	130.2
QI	0.2	0.3	0.2	4.9	3.9	3.8	4.4	10.4
TI	13	15.4	18.9	30.5	19.6	21.5	26.8	35.3
CV	50.3	50.5	52.3	58.1	53.6	55.8	58.8	62

Pitch	TM9	TM13	TM11	TM12	TM14	TM17	TM15	TM16
Treatment								
% topped coal tar	79.7	79.7	79.7	79.7	90.8	90.8	90.8	90.8
Duration	6	6	6	6	6	6	6	6
Temperature	350	370	385	410	350	370	385	410
Yield								
After topping	81.3	81.3	81.3	81.3	80.6	80.6	80.6	80.6
After treatment	81.2	79.3	78.2	74.0	79.7	79.6	78.2	73.9
Pitch yield	56.7	55.0	56.6	59.6	52.7	55.7	55.1	61.3
Analytical								
SP	114	121.3	122.7	123.7	124.7	116.9	124.6	128
QI	5.7	5.8	5.9	8.8	6.6	6.6	6.7	11.3
TI	21.1	25.5	27.8	32.7	24.7	24.6	28.1	36.2
CV	55.7	58.4	59	60.2	59.4	58.2	60.9	63.4

Pitch	TC5	TC8	TC6	TC7	TM8
Treatment					
% topped coal tar	100	100	100	100	79.7
Duration	6	6	6	6	6
Temperature	350	370	385	410	370
Yield					
After topping	80.1	80.1	80.1	80.1	81.3
After treatment	79.5	78.8	78.8	75.6	73.9
Pitch yield	54.7	57.1	58.4	61.5	62.7
Analytical					
SP	117.6	111.9	108.6	106.9	111.7
QI	7	6.7	6.6	7.1	7.8
TI	24.7	25.3	24.8	28	31.2
CV	59.4	56.6	56.8	55.3	58.2

Appendix C: Analytical Data of Straight Distilled Pitches

The tar feedstocks which have been used for thermal treatment (Chapter 2) were straight distilled to determine the influence of the softening point on yield, TI, and CV. Tables C-1 to C-6 contain the data obtained by these experiments.

SP	Yield	QI	TI	CV
103.6	70.9	0.1	3.9	40.0
111.5	68.7	0.1	4.6	41.8
122.4	65.9	0.1	3.7	43.6
133.5	62.6	0.1	4.9	46.3
154.2	56.8	0.1	8.9	51.2

Table C-1: Straight distillation of petroleum tar F98015.

SP	Yield	QI	TI	CV
32.8	85.8	0.1	5.7	30.7
84.6	68.5	0.1	7.0	39.0
110.5	60.6	0.1	8.5	43.9
115.4	59.0	0.1	8.9	45.8
129.1	55.6	0.1	10.1	49.2
146.0	51.6	0.1	11.9	52.1

Table C-2: Straight distillation of topped petroleum tar F98020.

SP	Yield	QI	TI	CV
104.3	59.5	3.4	13.7	48.4
110.8	57.5	3.6	14.3	50.1
120.2	54.8	3.7	15.6	52.0
133.3	51.4	3.9	16.5	55.1
175.6	41.8	4.7	23.5	66.7

Table C-3: Straight distillation of 50% topped petroleum tar / 50% topped coal tar.

SP	Yield	QI	TI	CV
86.1	63.8	4.6	15.3	46.3
100.7	58.3	5.0	16.7	50.3
109.2	55.5	5.2	18.0	53.2
117.9	53.4	5.5	20.2	55.3
126.8	50.9	5.7	21.2	59.2
145.1	46.2	6.3	25.6	62.2

Table C-4: Straight distillation of 20% topped petroleum tar / 80% topped coal tar.

SP	Yield	QI	TI	CV
100.8	58.4	5.6	18.2	52.3
115.8	54.1	6.0	19.6	56.0
119.8	53.3	6.4	21.6	57.1
128.6	51.1	6.6	22.9	59.0
147.1	46.7	6.8	27.7	65.3

Table C-5: Straight distillation of 10% topped petroleum tar / 90% topped coal tar.

SP	Yield	QI	TI	CV
109.6	56.4	6.7	54.9	20.1
122.7	52.0	7.2	58.8	23.3
131.7	49.8	7.7	62.8	25.7
169.9	41.3	9.4	72.8	34.6
87.1	63.3	6	50.0	17.8
99.2	58.9	6.2	53.1	19.0
106.2	56.9	6.4	54.9	20.3
115.5	54.1	6.5	57.6	21.8
124.7	51.5	7.2	60.7	24.8
152.0	44.8	7.9	68.9	32.4

Table C-6: Straight distillation of topped coal tar.

The data was fitted by second-degree polynomials. The coefficients to Equation C-1 are given in Tables C-7 to C-9. It was found that the coking value was best fitted by a linear regression.

$$Y(SP) = a * SP^2 + b * SP + c$$ Equation C-1

Y(SP)	Calculated response (yield, coking value or toluene insoluble)
a, b, c	Fitted coefficients
SP	Softening point

Sample	a	b	c	R^2	SP range
PT	0,000594	-0,4547	108,6	0,9935	84-144
TPT	0,000589	-0,4090	98,6	0,9999	84-146
TM50	0,000717	-0,4487	98,4	1,0000	104-175
TM80	0,001297	-0,5936	105,1	0,9994	86-145
TM90	0,000736	-0,4350	94,8	0,9997	100-147
TC	0,001076	-0,5483	103,3	1,0000	46-170

Table C-7: Coefficients to equation C-1 for yield. The equation is valid within the given softening point range.

Sample	a	b	c	R^2	SP range
PT	0	0,2201	17,1	0,9982	84-144
TPT	0	0,2192	20,3	0,9958	84-146
TM50	0	0,2567	21,4	0,9988	104-175
TM80	0	0,2795	22,5	0,9924	86-145
TM90	0	0,2790	23,8	0,9954	100-147
TC	0	0,2871	24,5	0,9962	46-170

Table C-8: Coefficients for coking value.

Sample	a	b	c	R^2	SP range
TPT	0,000603	-0,0592	7,7	1,0000	84-146
TM50	0,000809	-0,0906	14,4	0,9984	104-175
TM80	0,001311	-0,1265	16,4	0,9970	86-145
TM90	0,001993	-0,2859	26,7	0,9923	100-147
TC	0,002380	-0,3322	28,5	0,9859	46-170

Table C-9: Coefficients for toluene insoluble.

Equation C-1 is used to correct the yield, TI and CV of the pitches produced from thermally treated topped tars (Equations C-2 to C-4).

$$\mathrm{Yield}(SP_{ref}) = \mathrm{Yield}_{exp}\left[\frac{\mathrm{Yield}_{SD}(SP_{ref})}{\mathrm{Yield}_{SD}(SP_{exp})}\right] \qquad \text{Equation C-2}$$

$\mathrm{Yield}(SP_{ref})$ Yield corrected to a reference softening point (i.e. SP_{ref}=120°C)
Yield_{exp} Pitch yield found experimentally for tar treated pitch
$\mathrm{Yield}_{SD}(SP)$ Yield of straight distilled pitch with softening point SP (Equation C-1)
SP_{ref} Reference softening point (i.e. SP_{ref}=120°C)
SP_{exp} Softening point found experimentally for tar-treated pitch

Equations C-3 and C-4 give similar correction terms for the coking value and the toluene insoluble fraction.

$$CV(SP_{ref}) = CV_{exp}\left[\frac{CV_{SD}(SP_{ref})}{CV_{SD}(SP_{exp})}\right]$$ Equation C-3

$CV(SP_{ref})$ CV corrected to a reference softening point (i.e. SP_{ref}=120°C)
CV_{exp} CV found experimentally for tar treated pitch
$CV_{SD}(SP)$ CV of straight distilled pitch with softening point SP (Equation C-1)
SP_{ref} Reference softening point (i.e. SP_{ref}=120°C)
SP_{exp} Softening point found experimentally for tar-treated pitch

$$TI(SP_{ref}) = TI_{exp}\left[\frac{TI_{SD}(SP_{ref})}{TI_{SD}(SP_{exp})}\right]$$ Equation C-4

$TI(SP_{ref})$ TI corrected to a reference softening point (i.e. SP_{ref}=120°C)
TI_{exp} TI found experimentally for tar treated pitch
$TI_{SD}(SP)$ TI of straight distilled pitch with softening point SP (Equation C-1)
SP_{ref} Reference softening point (i.e. SP_{ref}=120°C)
SP_{exp} Softening point found experimentally for tar-treated pitch

Appendix D: Data Corrected to Standard Softening Point

In this appendix corrected data for experimentally produced pitches is presented. The pitches were given codes after the precursor material and the order of which they were produced. The following series were made:

K* Pitch produced from the petroleum tar F98015
TP* Pitch produced from the topped petroleum tar F98020
TC* Pitch produced from the topped coal tar F98017A
TM* Pitch produced from blends of the topped petroleum tar F98020 and the topped coal tar F98017A

The data is presented in tables which are built up according the following structure:

Table entry	**Unit**	**Explanation**
Pitch	-	Pitch code
Treatment		
Duration	hours	Duration of thermal treatment
Temperature	°C	Temperature of thermal treatment
Calculated		
Yield (110)	% (w/w)	Calculated yield of a 110°C SP pitch
Yield (120)	% (w/w)	Calculated yield of a 120°C SP pitch
CV (110)	% (w/w)	Calculated yield of a 110°C SP pitch
CV (120)	% (w/w)	Calculated yield of a 120°C SP pitch

Pitch	K3	K15	K1	K10	K16	K14	K5	K11
Treatment								
Duration	6	6	6	6	6	6	6	6
Temperature	307	307	312	330	330	346	349	363
Calculated								
Yield (110)	64.3	63.6	59.7	62.5	60.9	59.0	61.1	60.2
Yield (120)	61.1	60.5	56.8	59.5	58.0	56.2	58.1	57.3
CV (110)	44.4	44.2	45.4	46.0	45.7	48.6	48.1	49.0
CV (120)	46.8	46.5	47.8	48.4	48.1	51.2	50.7	51.6

Pitch	K12	K13	K6	K8	K7	K9	K17	K18
Treatment								
Duration	6	6	6	6	6	6	6	6
Temperature	365	369	370	370	390	390	392	415
Calculated								
Yield (110)	60.2	59.2	60.0	60.1	59.6	62.4	61.2	65.1
Yield (120)	57.3	56.3	57.1	57.2	56.7	59.4	58.2	62.0
CV (110)	49.3	50.4	50.6	49.8	53.4	51.8	52.0	53.0
CV (120)	51.9	53.1	53.3	52.5	56.2	54.6	54.8	55.8

Pitch	K20	K29	K27	K21	K30	K23	K24	K25	K26
Treatment									
Duration	0	0.5	1	2	4	6	8	12	16
Temperature	-	360	360	360	360	360	360	360	360
Calculated									
Yield (110)	65.0	62.7	62.8	59.8	59.9	59.6	59.8	59.8	61.3
Yield (120)	61.8	59.6	59.7	56.9	57.0	56.7	56.9	56.9	58.3
CV (110)	42.2	45.4	44.5	49.5	49.5	49.1	49.4	49.8	49.9
CV (120)	44.4	47.8	46.9	52.1	52.1	51.7	52.0	52.5	52.5

Pitch	TP1	TP3	TP4	TP5	TM4	TM7	TM1	TM3
Treatment								
% topped coal tar	0	0	0	0	50.1	50.1	50.1	50.1
Temperature	350	370	385	410	350	370	385	410
Calculated								
Secondary QI	0.2	0.3	0.2	4.9	0.5	0.2	1.0	7.2
TI (120)	13.0	16.3	19.7	28.1	20.1	21.4	25.4	32.8
CV(120)	50.3	52.0	53.5	55.8	54.6	55.6	56.6	59.0
Yield (120)	55.1	54.7	54.7	58.2	54.3	52.7	57.6	60.8

Pitch	TM9	TM13	TM11	TM12	TM14	TM17	TM15	TM16
Treatment								
% topped coal tar	79.7	79.7	79.7	79.7	90.8	90.8	90.8	90.8
Temperature	350	370	385	410	350	370	385	410
Calculated								
Secondary QI	0.4	0.4	0.6	3.8	0.1	0.5	0.5	5.7
TI (120)	22.3	25.2	27.1	31.6	23.6	25.3	26.9	33.5
CV(120)	57.4	58.0	58.2	59.1	58.1	59.1	59.6	61.0
Yield (120)	54.9	55.4	57.4	60.8	53.9	54.8	56.4	63.7

Pitch	TC5	TC8	TC6	TC7	TM8
Treatment					
% topped coal tar	100	100	100	100	79.7
Temperature	350	370	385	410	410
Calculated					
Secondary QI	0.1	0.1	0.2	1.0	3.0
TI (120)	25.3	27.4	27.7	31.8	33.7
CV(120)	60.1	58.9	60.1	59.1	60.7
Yield (120)	54.0	54.6	54.9	57.2	59.9

Appendix E: Elemental Composition of Pitch

This appendix lists the elemental composition of selected pitches. The data was measured by the commercial laboratory DBLab, Odense. Carbon, hydrogen, nitrogen and sulfur were analyzed on all the samples, while oxygen was measured on half of the samples. It was attempted to calculate the oxygen content by Equation E-1 for all of the samples but the precision of the measurement was not high enough for this calculation to yield a plausible result.

$$O(cal) = 100\% - \%C - \%H - \%N - \%S \qquad \text{Equation E-1}$$

Code	% CT	Temp.	C	H	N	S	O (ana.)	O (cal.)
Unit	%(w/w)	(°C)	%(w/w)	%(w/w)	%(w/w)	%(w/w)	%(w/w)	%(w/w)
F99004C	0	None	93.79	6.18	0.30	0.45		-0.72
TP1	0	350	93.46	5.99	0.30	0.49		-0.24
TP3	0	370	93.43	6.00	0.30	0.43		-0.16
TP4	0	385	93.26	5.83	0.28	0.50		0.13
TP4	0	385	94.01	5.81	0.28	0.46	0.40	-0.56
TP5	0	410	93.36	5.48	0.28	0.50		0.38
TM1	50	385	93.78	4.99	0.86	0.41		-0.04
F99007D	80	None	93.58	4.70	1.19	0.44	0.91	0.09
TM9	80	350	93.87	4.68	1.20	0.41	0.74	-0.16
TM13	80	370	93.78	4.55	1.23	0.40	0.69	0.04
TM11	80	385	93.72	4.75	1.20	0.41		-0.08
TM11	80	385	93.79	4.56	1.18	0.36	0.64	0.11
TM12	80	410	94.00	4.49	1.20	0.32	0.59	-0.01
TM15	90	385	93.98	4.56	1.30	0.41		-0.25
F99002B	100	None	93.54	4.36	1.39	0.42	0.87	0.29
TC5	100	350	93.36	4.40	1.42	0.42	0.87	0.40
TC8	100	370	93.62	4.44	1.39	0.39	0.85	0.16
TC6	100	385	93.22	4.55	1.40	0.43		0.40
TC6	100	385	93.36	4.50	1.40	0.41	0.90	0.33
TC7	100	410	92.96	4.51	1.39	0.37	0.89	0.77

Table E-1: Elemental composition of pitch.

Code	% CT	Temp.	H/C	N/C	S/C	O/C
Unit	%(w/w)	(°C)	Mol/mol	Mol/mol	Mol/mol	Mol/mol
F99004C	0	None	0.79	0.0027	0.0018	
TP1	0	350	0.76	0.0028	0.0020	
TP3	0	370	0.77	0.0028	0.0017	
TP4	0	385	0.74	0.0026	0.0020	
TP4	0	385	0.74	0.0026	0.0018	0.0032
TP5	0	410	0.70	0.0026	0.0020	
TM1	50	385	0.63	0.0079	0.0016	
F99007D	80	None	0.60	0.0109	0.0018	0.0073
TM9	80	350	0.59	0.0110	0.0016	0.0059
TM13	80	370	0.58	0.0112	0.0016	0.0055
TM11	80	385	0.60	0.0110	0.0016	
TM11	80	385	0.58	0.0108	0.0014	0.0051
TM12	80	410	0.57	0.0109	0.0013	0.0047
TM15	90	385	0.58	0.0119	0.0016	
F99002B	100	None	0.56	0.0127	0.0017	0.0070
TC5	100	350	0.56	0.0130	0.0017	0.0070
TC8	100	370	0.57	0.0127	0.0016	0.0068
TC6	100	385	0.58	0.0129	0.0017	
TC6	100	385	0.57	0.0129	0.0016	0.0072
TC7	100	410	0.58	0.0128	0.0015	0.0072

Table E-2: Molar composition of pitch relative to atomic carbon.

Appendix F: Metals in Pitch

Sample	% coal tar	HT temp.	S	Al	Ca	Fe	Mg	Mn	Na	Ni	Pb	Zn
	% (w/w)	°C	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
TP1	0	350	0.53	7	12	33	1	1	2	4	1	1
TP3	0	370	0.56	6	12	90	3	1	2	7	1	1
TP4	0	385	0.76	0	0	16	3	2	2	8	2	2
TP5	0	410	0.58	8	5	31	1	1	14	16	1	2
TM4	50	350	0.60	49	42	100	14	2	68	5	108	116
TM7	50	370	0.50	42	35	107	6	2	71	5	111	118
TM1	50	385	0.48	45	35	95	6	2	70	5	107	119
TM3	50	410	0.50	47	35	510	5	10	98	75	101	106
TM9	80	350	0.47	66	44	106	8	2	112	3	156	164
TM13	80	370	0.49	64	40	152	10	3	128	6	169	183
TM11	80	385	0.46	64	46	121	9	2	122	3	163	174
TM12	80	410	0.46	58	45	126	7	3	129	10	137	141
TM14	90	350	0.44	96	73	138	11	3	153	3	180	198
TM17	90	370	0.50	81	51	172	11	3	144	5	192	209
TM15	90	385	0.45	87	56	148	10	3	154	4	187	199
TM16	90	410	0.39	72	44	131	9	3	129	3	161	178
TC5	100	350	0.45	92	81	135	20	3	153	3	197	242
TC8	100	370	0.47	75	62	197	15	3	155	3	210	235
TC6	100	385	0.45	79	51	128	10	3	148	3	188	237
TC7	100	410	0.43	67	47	151	10	3	142	5	178	205

Table F-1: Metal content of pitch.

Appendix G: GC Analysis of Volatile Fraction of Topped Tar

Analysis of the tar oils was conducted in the Harmarville Technical Center. The applied GC was a Perkin Elmer model Autosystem equipped with a FID detector and a 30 meter SPB5 capillary column, 0.32mm in diameter and with 0.25 μm film thickness and helium as carrier. The temperature program was 40°C, 5 minutes hold time, ramp 5°C/min to 100°C, ramp 10 °C/min to 310 °C, hold time 30 minutes.

The applied GC-MS was a Perkin Elmer model Autosystem XL equipped with a Q-Mass 910 mass spectrometer detector and using helium as carrier gas. The column was a capillary column SP5 of 60 meters, 0.25 mm in diameter and with 0.25 μm film thickness. The temperature program was 40°C, 1 minute hold time, ramp 5°C/min to 100°C, ramp 2 °C/min to 310 °C, hold time 30 minutes.

Identified components are listed in Tables G-1 and G-2. The increase index (I_{GC}) was calculated by Equation G-1. The boiling points were found in the book by Anderson et al., 1963.

$$I_{GC} = \frac{Area_{HT} - Area_{Straight}}{Area_{Straight}} \qquad \text{Equation G-1}$$

I_{GC} Index of increase

$Area_{HT}$ Area of the peak in chromatogram of the heat-treated oil

$Area_{Straight}$ Area of the peak in chromatogram of the straight distilled oil

GC Rt. (Min.)	GC-MS Rt. (Min.)	I_{GC}	Boiling point (°C)	Component name
12.2			181.839	Phenol
14.0	20.3	5.7	177.82	Indan
14.8	20.8		191.003	O-cresol
15.3	21.6		201.94	P-cresol
15.5	22.3		202	5-methylindan
17.6	24.8		205.5	4-methylindan
21.8	30.1	-0.3	237.3	Quinoline
23.0	31.3	-0.2	243.25	Isoquinoline
25.5	33.6	0.2	241.052	2-methylnaphthalene
26.7	34.6	0.2	244.685	1-methylnaphthalene
30.3	38.6	-0.1	255	Biphenyl
31.6	41.1	0.0	262	2,6-dimethylnaphthalene, 2,7-dimethylnaphthalene
31.6	41.3	0.0	263	1,6-dimethylnaphthalene, 1,7-dimethylnaphthalene
32.1	42.2	0.1	265	1,3-dimethylnaphthalene, 1,5-dimethylnaphthalene
32.5	43.1	-0.2	268.5	1,2-dimethylnaphthalene, 1,4-dimethyl-naphthalene, 2,3-dimethylnaphthalene
36.1	54.1	0.2	305.5	2-methyldibenzofuran
36.5	55.0	2.3	293	4,4-dimethylbiphenyl
36.7	56.2	1.3	305	x,x-dihydroanthracene
36.9	56.9	2.0	312	9,10-dihydroanthracene
37.1	57.5	0.5	317.9	2-methylfluorene
37.8	60.7	1.1	331.4	Dibenzothiophene
38.5	64.5	-0.5	343.9	Acridine
38.7	65.4	0.3	350	Benzoquinoline
39.6	69.7	0.3	351.5	3-methylphenanthrene
39.7	69.7	0.3	353	4H-cyclopenta(d,e,f)phenanthrene
39.8	69.7	0.1	354	9-methylphenanthrene, 2-methylphenanthrene
39.9	69.9	0.1	358.6	2-methylanthracene, 1-methylphenanthrene
40.0	70.2	0.3	363	1-methylanthracene
40.5	71.9	0.3	334	1-phenylnaphthalene
42.3	80.6	-0.5	345	2-phenylnaphthalene
42.3	80.8	0.4	387.7	Benzo(b)naphtho(2,1-d)furan
43.1	83.6	0.4	401.6	2,3-benzofluorene
43.3	84.7	0.1	407	1,2-benzofluorene
43.3	84.9	0.2	410	1-methylpyrene
44.0	87.3	-0.2	414.5	5,12-dihydronaphthacene
44.2	88.3	0.4	396	Dimethylpyrene
44.8	89.8	-0.1	429.9	Benzo(b)naphtho(2,1-b)thiophene
45.3	92.9	-0.4	437.5	Benz(a)anthracene
45.6	95.5	-0.7	440	Benzo(b)naphtho(2,3-d)thiophene

Table G-1: Identified components in coal-derived material.

GC Rt. (Min.)	GC-MS Rt. (Min.)	I_{GC}	Boiling point (°C)	Component name
13.971	20.27	4.1	177.82	Indan
19.296	27.37	13.2	217.955	Naphthalene
30.316	38.68	-0.3	255	Biphenyl
30.811	39.8	-0.2	258.67	1-ethylnaphthalene
31.594	41.59	-0.2	262	2,6-dimethylnaphthalene, 2,7-dimethylnaphthalene
31.675	41.89	-0.2	263	1,6-dimethylnaphthalene, 1,7-dimethylnaphthalene
32.481	43.48	-0.5	270	2-methyl-6-ethylnaphthalene
33.184	45.23	-0.3	270	Acenaphthylene
33.287	45.29	-0.2	272.7	3-methylbiphenyl
33.474	46.35	-0.2	277	2,3,6-trimethylnaphthalene, 1,2,7-trimethylnaphthalene
33.698	47.44	1.4	280	1,2,6-trimethylnaphthalene, 1,3,6-trimethylnaphthalene, 1,3,7-trimethylnaphthalene
33.821	47.7	-0.3	289	2,3,5-trimethylnaphthalene
35.191	51.17	6.1	297.2	Fluorene
38.233	62.46	0.3	339.6	Phenanthrene
38.337		-0.1	339.77	Anthracene
39.657	68.06	0.5	351.5	3-methylphenanthrene
39.734	68.66	0.5	354.8	2-methylphenanthrene

Table G-2: Identified components in petroleum-derived material.

Appendix H: Testing Procedures for Anodes

H.1. Density Measurements

H.1.1. Green Apparent Density

Green apparent density (GAD) is in real life mainly measured because of the early indication it gives of the baked apparent density. Roughly, the GAD will increase with the pitch level until the optimum pitch level is reached, after which the GAD will level off at a constant level. Early warning of under-pitching can be obtained by monitoring the GAD of the anodes.

For the laboratory-scale, cylindrical anode blocks, the green density was measured in the following way. The height of the anode was measured three times with a pair of electronic calipers (±0.001 cm) turning the block 120° for each measurement. The diameter of the block was measured one centimeter from each end and at the center of the anode, each time by turning the block 90°. The sample was weighed with a precision of ±0.1 gram. The GAD can be calculated from Equation H-1.

$$GAD = \frac{4W}{\pi D_a^2 H_a} \qquad \text{H-1}$$

GAD: Green apparent density (g/cm^3)
W: Weight of anode (g)
D_a: Average diameter of anode (cm)
H_a: Average height of anode (cm)

H.1.2. Baked Apparent Density (Block)

The baked apparent density (BAD) is considered to be a very important property of the anode. First of all, BAD indicates the amount of carbon in each anode thus giving estimates of lifetime and efficiency. Secondly, it is relatively simple to measure. Most

other analytical properties are at their optimum at pitching levels close to the optimum pitching level of BAD.

This measurement was performed in the same way as for the GAD. The main sources of error were fluid coke sticking to the surface and swelling of the anode during baking, which could give an irregular shape. The BAD is calculated by Equation H-2.

$$BAD = \frac{4W}{\pi D_a^2 H_a} \qquad \text{H-2}$$

BAD: Baked apparent density (g/cm^3)
W: Weight of anode (g)
D_a: Average diameter of anode (cm)
H_a: Average height of anode (cm)

H.1.3. In Situ Coking Value

The in situ coking value is the true coking value of the pitch measured under actual anode manufacture conditions. In situ CV is calculated from the anode weight before and after baking by the assumption of unchanged mass of the coke.

H.1.4. Shrinkage

The volume of the anode might change during baking. The shrinkage is calculated from the anode volume before and after baking.

H.1.5. Baked Apparent Density (core)

After a core had been obtained from the anode block the BAD is measured again. This BAD can be determined with greater accuracy due to the higher regularity of the sample and the total removal of fluid coke sticing to the surface during baking. Apart from the smaller size, the BAD of the core is measured in exactly the same way as on the block.

H.1.6. True Density

The true density is the density of the carbon matrix in the anode without pores and cavities. It gives some information about the carbon structure.

The true density was measured by a penta-pycnometer from Quata Chrome. The measurement was based on Archimedes' principle. The sample was ground by a Herzog grinder mill to assure that there was no inaccessible porosity left in the sample. The ground sample was dried at 130°C for a minimum of four hours and 6.5-7 grams of sample were placed in the measuring cell. The sample cell was purged with helium and then put under a helium pressure of 1.12 bars above atmospheric pressure. The pressure was released into a reference cell held at atmospheric pressure and the two cells were allowed to equilibrate. The sample volume was calculated from Equation H-3 and the true density by Equation H-4.

$$V_{sample} = V_{cell} + \frac{V_{ref}}{1 - \frac{P_1 - P_a}{P_2 - P_a}} \qquad \text{H-3}$$

V_{sample}: Volume of the sample
V_{cell}: Volume of the measuring cell
V_{ref}: Volume of the reference cell
P_1: Pressure before the helium is relieved into the reference cell
P_2: Pressure after the helium is relieved into the reference cell
P_a: Atmospheric pressure

$$d_{true} = \frac{m_{sample}}{V_{sample}} \qquad \text{H-4}$$

d_{true}: True density
m_{sample}: Mass of sample

H.2. Electrical Resistivity

Electrical resistivity is one of the prime properties measured on the anodes. It is significant for power consumption and current efficiency in the production of aluminum.

The measurement was conducted on a core which was 130 mm in height and 50 mm in diameter. The core was fixed between two copper plates and six amperes of current were supplied over the sample by a Power Design constant current/constant voltage instrument. A probe with two contact points placed 100 mm apart was placed on the sample offering an alternative route for the current and the drop in voltage was recorded. The measurement was repeated at points with a 90° angle and the current was reversed to measure a total of eight positions. The electrical resistivity is given in μΩm and can be calculated by Equation H-5:

$$ER = \frac{\Delta V \; A_{sample}}{L_{probe} \; I} \qquad \text{H-5}$$

ER: Electrical resistivity
ΔV: Average drop in voltage
A_{sample}: Average cross section of sample
L_{probe}: Probe length
I: Current supplied over the sample

H.3. Air Permeability

The air permeability of an anode core has significance for the intrusion of gases (and therefore unwanted reactivity) in the sample. The permeability of the anode should be as low as possible.

Air permeability was measured by an AP-50 Air Permeability Apparatus (R&D Carbon Ltd., Sierra, Switzerland). The sample was prepared by cutting it to a diameter of 50 mm and a length of 20 mm. The sample was placed in a sample holder and a seal around the sample was obtained by applying a 3.5 bar pressure to a rubber membrane surrounding the entire height of the sample. A vacuum was created under the sample and the time it took the vacuum to be released through the sample was recorded, giving the estimate of the air

permeability. The result was calculated by the apparatus in nPm (1 darcy = 9.81 nPm). The measurement was repeated twice from each side of the anode disk.

H.4. Strength of the Anode

Strength measurements were performed on an ATS Universal Testing Machine, Model No. 1230. It has a load cell capacity of 10000 and 30000 pounds and is manufactured by Applied Test Systems, Butler, Pennsylvania.

H.4.1. Flexural Strength

Flexural energy is also referred to as bending energy. It measures the ability of the anode to withstand a three-point load.

The sample (50 mm in diameter × 130 mm in length) was placed on two metal bars (∅ 6 mm) 100 mm apart. A top load cell consisting of a metal bar of 6 mm in diameter, applied force to the center of the sample. The top load cell was lowered with a velocity of 5 mm/minute until the sample fractured. The flexural strength is calculated from Equation H-6.

$$Flex.\ strength = \frac{8(F \times L)}{\pi\ D^3} \qquad \text{H-6}$$

F: Load of fraction (N)
L: Distance between supports
D: Diameter of sample
π: Phi

H.4.2. Fracture Energy

The fracture energy is measured with the same load cell as the flexural energy. The main difference is that this measurement concerns the energy necessary to propagate a fracture in a specific area. The sample was notched by making two cuts into the center of the

sample leaving an angle of 60° on the side of the anode (Figure H-1). The sample was placed so that the notched angle turned downwards. The top load cell was lowered with a velocity of 6 mm/minute until the sample fracture.

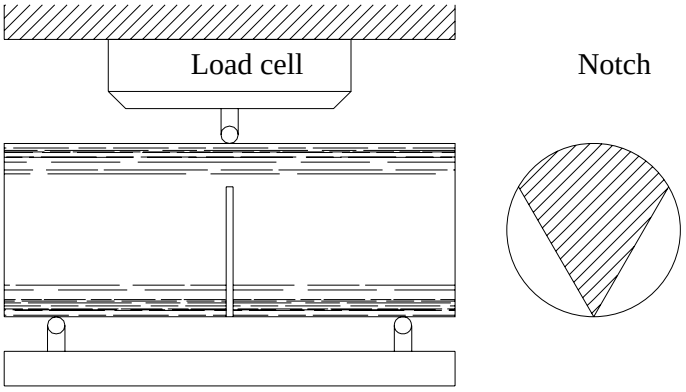

Figure H-1: Test arrangement for the fracture energy measurement (inspired by Fischer et al., 1995).

The fracture energy is calculated by Equations H-7 and H-8:

$$Fracture\ energy = \frac{1}{2A}\int_0^{ln} FdL \qquad \text{H-7}$$

A: Notched area
F: Load of fraction (N)
L: Deflection of sample center

The notched area can be calculated as

$$A = \frac{1}{3}\left[\frac{\pi D_A^2}{4} - \frac{D_B^2\sqrt{3}}{4}\right] + \frac{D_B^2\sqrt{3}}{4} \qquad \text{H-8}$$

D_A: Average diameter of core
D_B: Diameter of the notched area

H.4.3. Compressive Strength and Static Elasticity

This measurement determines the ability of the anode to withstand compressive loads. In the same measurement the static elasticity (Young's modulus) is determined.

The anode sample (50 mm in diameter × 50 mm in height) was placed between two compression plates. The upper load cell was lowered with a velocity of 12.7 mm/minute until the sample broke. The compressive strength is calculated by Equation H-9:

$$Comp.\,strength = \frac{4W}{\pi D^2} \qquad \text{H-9}$$

W: Total load on the sample at failure
D: Average diameter of sample

The static elasticity is defined as the initial slope of the stress (Pa) curve as a function of the strain (mm/mm). The modulus is determined by the calculated slope of the data ranging from 10 to 25 % of the peak stress.

H.5. Reactivity Measurements

H.5.1. Air Reactivity

The purpose of the anode is to conduct current to the reduction pot and to reduce alumina to aluminum. A part of the anode can, however, be lost by air burn. The air reactivity is a measure of how readily the anode reacts with air and how much of the anode is lost as dust by this process.

The analysis was conducted in a vertical temperature controlled muffling oven. The sample was a core of a diameter of 50 mm and a height of 60 mm with a 6.25 mm wide and 30 mm deep hole drilled from one of the ends. The sample was mounted on a vertical rod inside of the oven. While the oven was purged with nitrogen the temperature was raised to 550°C and allowed to equilibrate for one hour. The nitrogen flow was turned off and an air stream of 200 l/h was introduced while the oven was cooled at ramp of 15 °C/h to 400°C.

The rod with the sample was agitated frequently in order to shake off dust, which was collected in a dustpan. The air stream was terminated and the oven cooled to 300°C under a nitrogen purge.

Sample and dust were weighed after the reaction to estimate the direct weight loss. The sample was dusted with a brush placed in a ceramic ball mill with twenty 6×3/8 inch steel rods and tumbled for one minute (100 rotations). The residue was weighed and the amount of dust and anode residue was estimated.

H.5.2. CO_2 Reactivity

CO_2 is formed from the anode as part of the reduction of alumina to aluminum. The CO_2 is capable of reacting further with the anode forming CO. The reaction is responsible for a part of the anode consumption.

The CO_2 furnace held two samples at the same time. The samples (50mm in diameter × 60mm in height) were placed in horizontal holders with dustpans beneath and a control thermocouple between them. The samples were heated to 960°C under a stream of nitrogen. The nitrogen stream was terminated and a 107 l/h stream of CO_2 (0.3 volume changes per minute) was introduced. After seven hours the CO_2 was turned off and the samples were allowed to cool while the oven was purged with nitrogen. The samples were subsequently treated as described in Section H.5.1. and CO_2 residue, loss and dust were calculated.

H.6. Thermal Properties

H.6.1. Thermal Conductivity

Thermal conductivity is a measure of how well the anode transfers the heat. When a cold anode is placed in a cold bath, the thermal conductivity is a measure of the likelihood that the anode cracks as a result of the thermal shock.

The apparatus used for this measurement was a Quickline-10-C Thermal Impedance Tester manufactured by the Anter Laboratories, Pittsburgh. The sample was prepared by cutting it into a disk measuring 50 mm in diameter and 20 mm in height. It was fixed between two thermometer plates by applying a 0.28 bar pressure to the sample, which was put in series with a material of known thermal conductivity and the two materials were allowed to equilibrate. The temperature difference over the reference material was compared to that of the sample and the thermal conductivity was calculated in the equipment in the unit W/mK.

H.6.2. Coefficient of Thermal Expansion (CTE)

The thermal expansion gives a measure of how much stress an anode will experience as it is lowered into the hot smelter pot. The definition of the coefficient of thermal expansion is given in Equation H-10.

$$\alpha = \frac{1}{L}\frac{dL}{dT} \qquad \text{H-10}$$

α: Linear thermal expansion coefficient (CTE)
L: Length of the anode
dL: Change in length as a result of temperature change
dT: Temperature change

The coefficient of thermal expansion is a function of temperature and is given at 300°C. Two anode samples (50mm in diameter × 130mm in height) were placed in a temperature-controlled furnace. Each of them were mounted vertically in separate quartz tubes. A quartz rod, connected to electronic gauges, was placed on top of each sample. The furnace was heated to 300°C at a ramp of 2.5°C/minute. Software was developed to correlate the data by a polynomial and gave the coefficient of thermal expansion at 300°C.

Appendix I: Analytical Results of Anode Testing

The results of the anode testing procedures which were described in Appendix H are given in this appendix. The data is average values of all values obtained for the pitching level of a particular pitch. A summary of the pitch codes is given in Table I-1. Heat treatment refers to a six-hour treatment at 385°C as topped tar followed by distillation to pitch. The results are given in numerical form (Tables I-2 to I-21) and graphic form (Figures I-1 to I-20).

Blend	Treatment	Coal tar	Blend 80/20	Petroleum tar
Blended as pitch	Straight distilled	CTP_S	MIX_S	PP_S
	Heat treatment	CTP_{T1}	MIX_{T1}	PP_{T1}
Blended as topped tar	Heat treatment		MIX_{T2}	

Table I-1: Treatment of pitches.

Results

Pitching level	CTP_S	PP_S	MIX_S	CTP_{T1}	PP_{T1}	MIX_{T1}	MIX_{T2}
13		1.555	1.528		1.547		
14	1.548	1.594	1.576	1.559	1.595	1.561	1.556
15	1.598	1.623	1.619	1.587	1.622	1.610	1.605
16	1.627	1.627	1.645	1.642	1.621	1.627	1.638
17	1.648			1.652		1.640	1.638

Table I-2: Average green apparent densities measured on the anode block (g/cc).

Pitching level	CTP_S	PP_S	MIX_S	CTP_{T1}	PP_{T1}	MIX_{T1}	MIX_{T2}
13		1.473	1.472		1.481		
14	1.507	1.489	1.523	1.509	1.509	1.507	1.506
15	1.539	1.489	1.544	1.529	1.514	1.541	1.534
16	1.542	1.460	1.534	1.546	1.491	1.537	1.540
17	1.526			1.532		1.514	1.516

Table I-3: Average baked apparent densities measured on the anode block (g/cc).

Pitching level	CTP_S	PP_S	MIX_S	CTP_{T1}	PP_{T1}	MIX_{T1}	MIX_{T2}
13		52.8	65.9		59.0		
14	70.4	53.3	66.0	66.3	59.1	65.3	66.1
15	69.5	53.7	64.9	66.2	58.2	65.8	65.6
16	69.6	53.0	63.0	66.7	59.2	65.2	65.8
17	68.3			66.7		65.6	65.0

Table I-4: In situ coking value (%).

Pitching level	CTP_S	PP_S	MIX_S	CTP_{T1}	PP_{T1}	MIX_{T1}	MIX_{T2}
13		0.91	1.29		1.10		
14	1.37	-0.09	1.36	1.46	0.40	1.33	1.42
15	0.80	-1.37	0.33	1.34	-0.56	0.74	0.61
16	-0.37	-3.19	-1.24	-0.58	-1.51	-0.53	-0.48
17	-2.16			-1.68		-1.97	-1.57

Table I-5: Shrinkage (%).

Pitching level	CTP_S	PP_S	MIX_S	CTP_{T1}	PP_{T1}	MIX_{T1}	MIX_{T2}
13		1.487	1.488		1.492		
14	1.525	1.499	1.534	1.526	1.515	1.523	1.524
15	1.548	1.487	1.549	1.544	1.516	1.546	1.547
16	1.548	1.463	1.541	1.551	1.494	1.537	1.541
17	1.528			1.537		1.521	1.515

Table I-6: Average baked apparent densities measured on the anode core (g/cc).

Pitching level	CTP_S	PP_S	MIX_S	CTP_{T1}	PP_{T1}	MIX_{T1}	MIX_{T2}
13		2.061	2.052		2.057		
14	2.054	2.052	2.046	2.049	2.046	2.059	2.058
15	2.065	2.053	2.051	2.046	2.050	2.066	2.059
16	2.047	2.043	2.050	2.042	2.060	2.062	2.052
17	2.042			2.050		2.049	2.046

Table I-7: Average true densities (g/cc).

Pitching level	CTP_S	PP_S	MIX_S	CTP_{T1}	PP_{T1}	MIX_{T1}	MIX_{T2}
13		75.5	82.7		72.3		
14	67.9	71.2	66.1	68.1	65.3	68.0	66.7
15	60.4	76.5	60.8	61.0	65.4	60.3	60.5
16	59.4	76.1	62.5	60.9	64.1	61.5	62.1
17	61.0			61.1		61.6	61.7

Table I-8: Average electrical resistivity (µ Ohm m).

Pitching level	CTP_S	PP_S	MIX_S	CTP_{T1}	PP_{T1}	MIX_{T1}	MIX_{T2}
13		1.85	3.05		1.66		
14	1.73	1.14	0.67	1.13	0.75	0.96	1.00
15	0.63	2.01	0.50	0.79	0.96	0.37	0.42
16	0.66	4.48	0.81	0.55	1.90	0.71	0.68
17	1.23			0.84		1.35	1.53

Table I-9: Average air permeability (nPm).

Pitching level	CTP_S	PP_S	MIX_S	CTP_{T1}	PP_{T1}	MIX_{T1}	MIX_{T2}
13		3.37	1.98		2.52		
14	3.90	4.08	4.49	3.40	3.50	3.81	3.83
15	5.09	4.79	5.51	5.24	5.52	5.28	5.52
16	6.47	4.92	7.27	6.77	7.68	7.43	6.66
17	7.98			7.52		7.35	8.22

Table I-10: Average flexural strength (MPa).

Pitching level	CTP_S	PP_S	MIX_S	CTP_{T1}	PP_{T1}	MIX_{T1}	MIX_{T2}
13		105.8	43.8		67.7		
14	151.1	125.8	102.2	119.8	107.6	111.5	136.7
15	229.7	132.3	258.2	152.8	140.6	126.8	142.6
16	242.1	161.2	205.3	176.1	253.3	182.2	219.2
17	227.9			231.9		192.1	218.9

Table I-11: Average fracture energy (J/m^2).

Pitching level	CTP_S	PP_S	MIX_S	CTP_{T1}	PP_{T1}	MIX_{T1}	MIX_{T2}
13		28.58	33.46		33.08		
14	37.21	28.98	39.09	36.61	26.86	37.77	36.82
15	43.77	23.27	41.16	38.12	29.19	40.90	37.53
16	42.85	20.42	34.13	33.25	29.01	36.99	34.27
17	35.29			30.70		35.42	37.23

Table I-12: Average compressive strength (MPa).

Pitching level	CTP_S	PP_S	MIX_S	CTP_{T1}	PP_{T1}	MIX_{T1}	MIX_{T2}
13		1725.1	1908.1		1873.1		
14	1858.6	947.5	2614.2	1219.1	925.6	2423.4	2298.2
15	1891.3	1228.4	2649.8	1570.7	1347.2	2397.0	2064.0
16	2294.1	1148.7	1856.2	1019.1	1881.7	2302.8	2276.9
17	2609.3			1214.9		3120.0	2943.5

Table I-13: Average compressive elasticity (Young's modulus) (MPa).

Pitching level	CTP_S	PP_S	MIX_S	CTP_{T1}	PP_{T1}	MIX_{T1}	MIX_{T2}
13		24.93	24.09		24.55		
14	24.00	24.63	23.90	23.84	25.11	23.98	24.93
15	23.78	25.67	23.81	24.29	24.20	23.58	21.39
16	24.39	25.85	24.10	23.78	26.16	22.44	21.99
17	26.32			23.53		24.84	24.87

Table I-14: Average weight loss (%) from air reactivity measurement.

Pitching level	CTP_S	PP_S	MIX_S	CTP_{T1}	PP_{T1}	MIX_{T1}	MIX_{T2}
13		11.58	9.16		11.08		
14	6.25	12.73	7.39	7.95	11.52	7.15	8.00
15	6.02	14.95	6.02	7.71	10.64	7.38	7.29
16	7.09	15.36	6.65	6.71	12.12	8.18	8.06
17	6.98			7.03		7.02	8.18

Table I-15: Average dust (%) from air reactivity measurement.

Pitching level	CTP_S	PP_S	MIX_S	CTP_{T1}	PP_{T1}	MIX_{T1}	MIX_{T2}
13		63.48	66.76		64.36		
14	69.72	62.63	68.69	67.17	63.37	68.85	67.04
15	70.18	59.37	70.16	67.94	65.15	69.01	71.32
16	68.65	58.77	69.24	69.49	61.70	69.35	69.94
17	66.68			69.44		68.13	66.95

Table I-16: Average residue (%) from air reactivity measurement.

Pitching level	CTP_S	PP_S	MIX_S	CTP_{T1}	PP_{T1}	MIX_{T1}	MIX_{T2}
13		10.17	10.46		12.26		
14	9.44	9.89	8.70	8.53	10.32	11.40	10.82
15	9.55	9.30	9.58	9.88	10.73	8.98	10.26
16	8.82	10.37	9.86	9.81	10.34	10.04	10.38
17	12.81			10.57		10.16	11.33

Table I-17: Average weight loss (%) from CO_2 reactivity measurement.

Pitching level	CTP_S	PP_S	MIX_S	CTP_{T1}	PP_{T1}	MIX_{T1}	MIX_{T2}
13		3.13	2.94		3.93		
14	2.59	3.70	1.85	1.86	3.72	3.40	2.96
15	1.95	2.96	2.34	2.83	3.31	2.03	2.63
16	2.00	3.32	2.94	2.87	3.18	2.36	2.86
17	3.48			2.93		2.27	3.44

Table I-18: Average dust (%) from CO_2 reactivity measurement.

Pitching level	CTP_S	PP_S	MIX_S	CTP_{T1}	PP_{T1}	MIX_{T1}	MIX_{T2}
13		83.78	84.66		81.48		
14	86.16	84.30	87.78	88.42	83.58	83.34	83.38
15	86.50	85.40	86.16	85.48	84.72	86.49	85.63
16	87.30	82.62	85.38	85.75	84.24	85.01	84.81
17	79.73			84.54		85.93	83.94

Table I-19: Average residue (%) from CO_2 reactivity measurement.

Pitching level	CTP_S	PP_S	MIX_S	CTP_{T1}	PP_{T1}	MIX_{T1}	MIX_{T2}
13		2.23	2.21		2.51		
14	2.19	2.12	2.50	2.43	2.55	2.60	2.53
15	2.46	1.73	2.52	2.60	2.48	2.60	2.68
16	2.58	2.01	2.47	2.46	2.35	2.48	2.56
17	2.56			2.49		2.43	2.52

Table I-20: Average thermal conductivity (W/mK).

Pitching level	CTP_S	PP_S	MIX_S	CTP_{T1}	PP_{T1}	MIX_{T1}	MIX_{T2}
13		3.581	3.631		3.656		
14	3.800	3.718	3.578	3.684	3.607	3.744	3.709
15	3.773	3.661	3.755	3.716	3.660	3.722	3.733
16	3.792	3.647	3.759	3.689	3.672	3.721	3.718
17	3.707			3.778		3.757	3.642

Table I-21: Average coefficient of thermal expansion (CTE) (10^{-6} K^{-1} at 300°C).

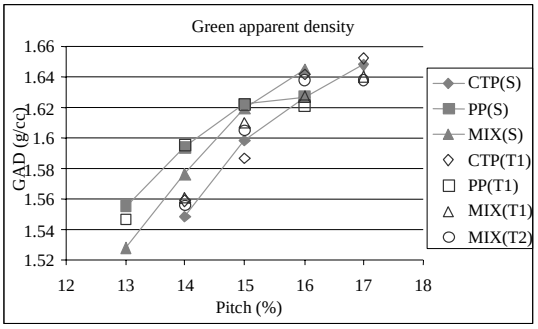

Figure I-1: Green apparent density as a function of pitching level.

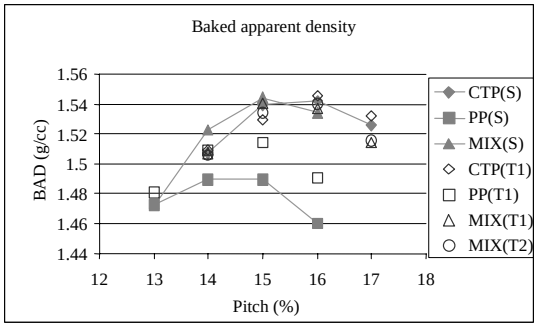

Figure I-2: Baked apparent density measured on the anode block as a function of pitching level

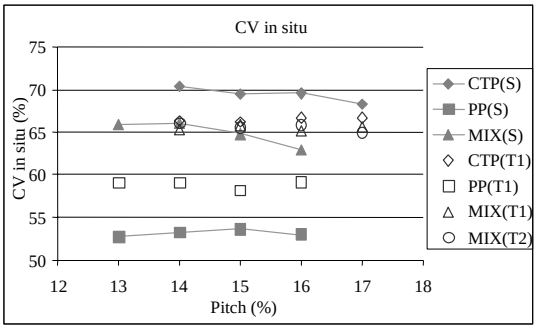

Figure I-3: In situ coking value (%) as a functions of pitching level.

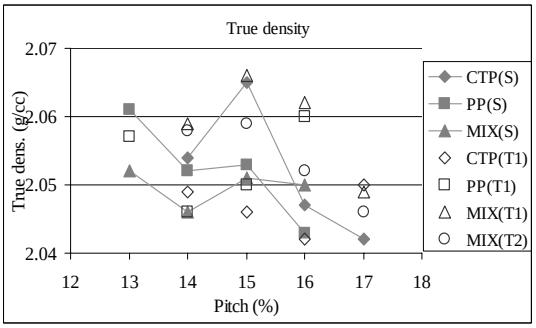

Figure I-6: Average true density (g/cc) as a function of pitching level.

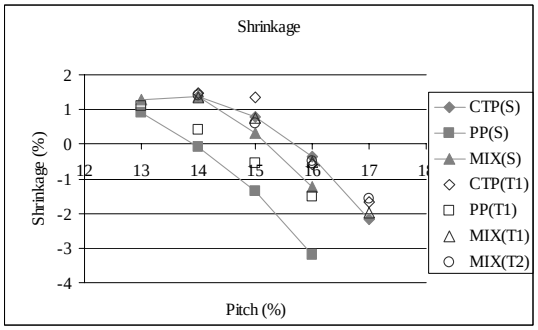

Figure I-4: Shrinkage (%) as a function of pitching level.

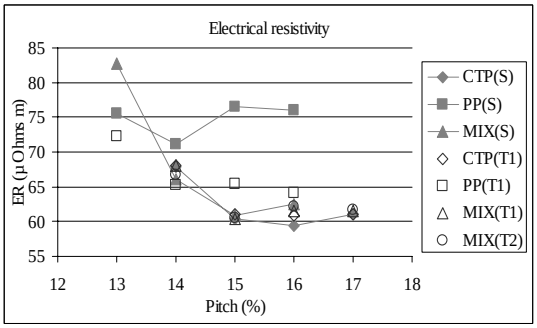

Figure I-7: Average electrical resistivity (µ Ohm m) as a function of pitching level.

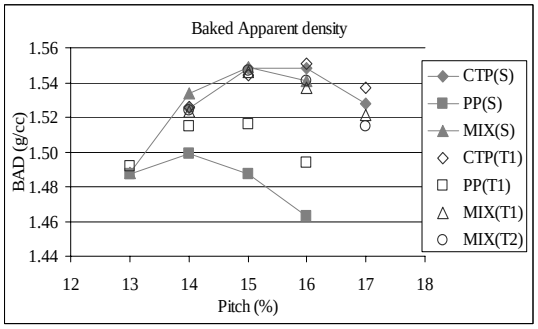

Figure I-5: Baked apparent density measured on the anode core as a function of pitching level

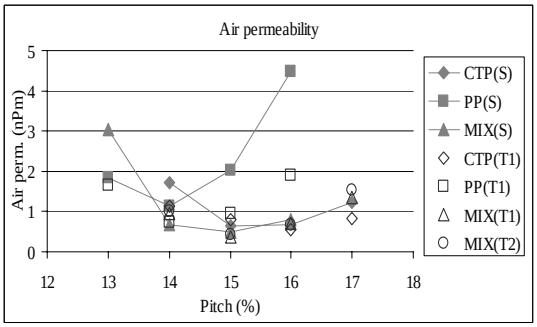

Figure I-8: Average air permeability (nPm) as a function of pitching level.

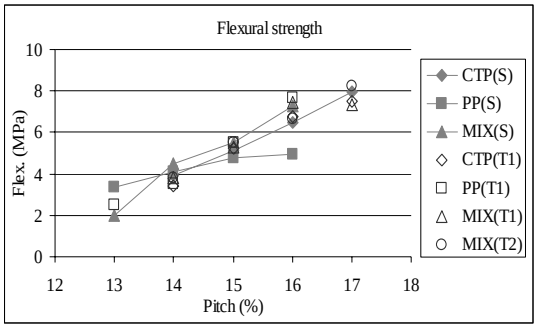

Figure I-9: Average flexural strength (MPa) as a function of pitching level.

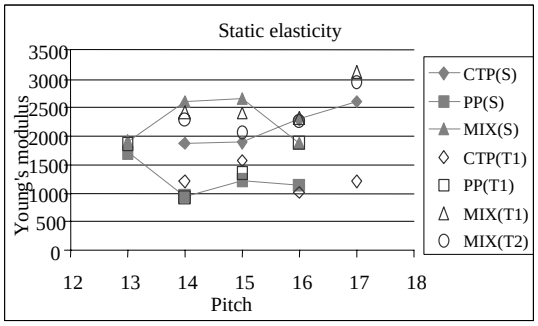

Figure I-12: Average static elasticity (Young's modulus) (MPa) as a function of pitching level.

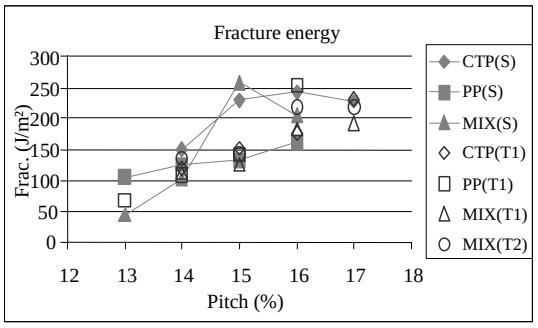

Figure I-10: Average fracture energy (J/m^2) as a function of pitching level.

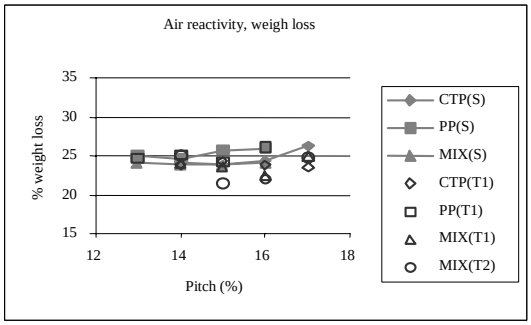

Figure I-13: Average weight loss (%) from air reactivity measurement as a function of pitch level.

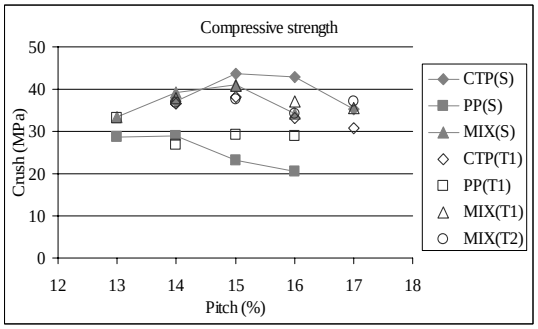

Figure I-11: Average compressive strength (MPa) as a function of pitching level.

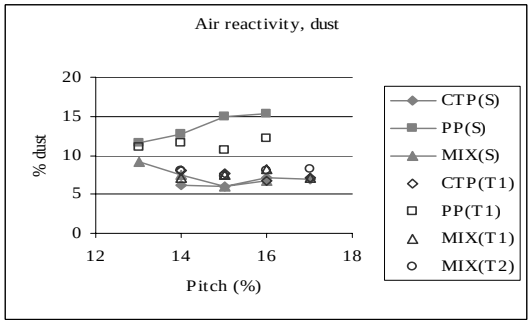

Figure I-14: Average dust (%) from air reactivity measurement as a function of pitch level

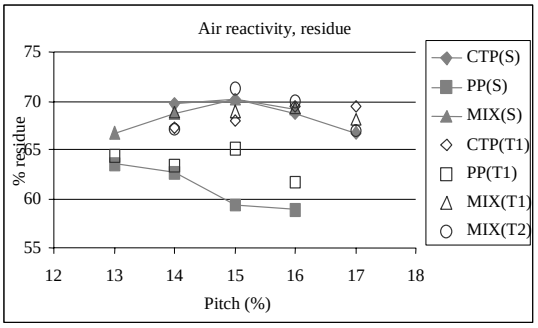

Figure I-15: Average residue (%) from air reactivity measurement as a function of pitch level.

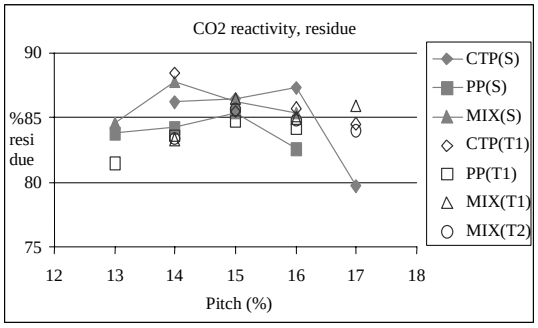

Figure I-18: Average residue (%) from CO_2 reactivity measurement as a function of pitch level.

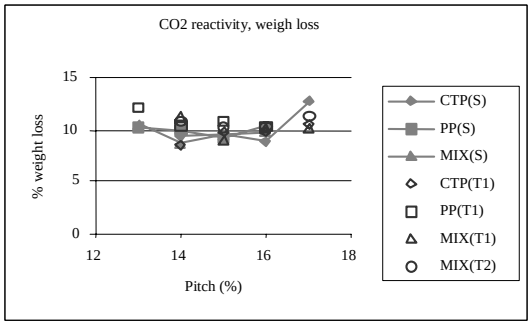

Figure I-16: Average weight loss (%) from CO_2 reactivity measurement as a function of pitch level.

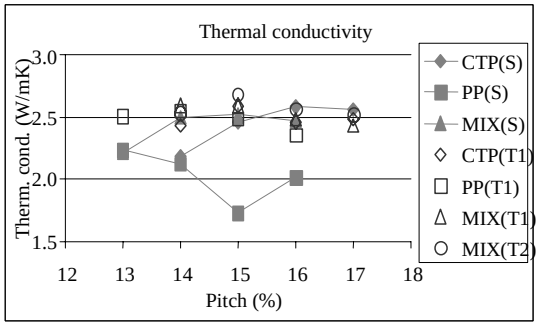

Figure I-19: Average thermal conductivity (W/mK) as a function of pitch level.

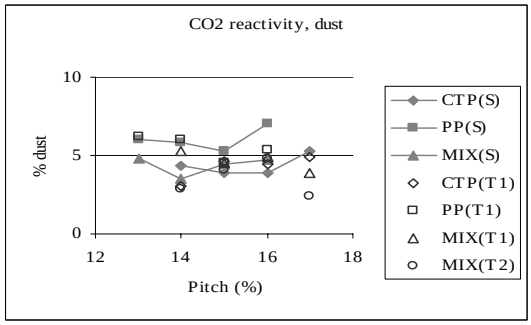

Figure I-17: Average dust (%) from CO_2 reactivity measurement as a function of pitch level.

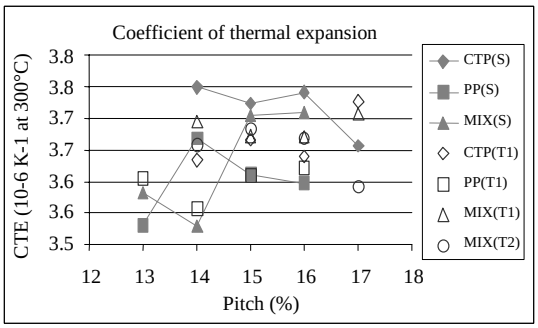

Figure I-20: Average coefficient of thermal expansion (CTE) (10^{-6} K^{-1} at 300°C) as a function of pitch level.

Appendix J: Correlation between Pitch Properties and Optimum Anode Properties

Correlation between the properties X and Y is defined by Equation J-1 and it is calculated using Equation J-2

$$\rho_{X,Y} = \frac{\mathrm{cov}(X,Y)}{\sigma_X \sigma_Y}$$ Equation J-1

$\rho_{X,Y}$ Correlation between X and Y

cov(X, Y) Covariance between X and Y

σ_X^2 Variance of X

σ_Y^2 Variance of Y

$$\rho_{X,Y} = \frac{\sum (x_i - \mu_X)(y_i - \mu_Y)}{\sqrt{\sum (x_i - \mu_X)^2 \sum (y_i - \mu_Y)^2}}$$ Equation J-2

x_i i'th value of x

μ_X Average value of x

y_i i'th value of y

μ_Y Average of value y

	%CT	SP	QI	TI	β-resin	CV(pitch)	Ash	Dens.
%CT	1							
SP	-0.19	1						
QI	0.99	-0.14	1					
TI	0.73	0.03	0.75	1				
β-resin	0.42	0.12	0.43	0.92	1			
CV(pitch)	0.85	-0.12	0.86	0.97	0.81	1		
Ash	0.97	-0.04	0.99	0.74	0.43	0.85	1	
Dens. (pitch)	0.97	-0.13	0.98	0.85	0.57	0.94	0.97	1

Table J1: Correlation between pitch properties (%CT: percentage of coal derived material, see Section 1.5 for abbreviations).

	%CT	SP	QI	TI	β-resin	CV(pitch)	Ash	Dens.
%pitch	0.76	-0.27	0.80	0.75	0.55	0.82	0.81	0.83
GAD	0.51	-0.14	0.61	0.63	0.50	0.64	0.61	0.63
BAD (block)	0.92	-0.26	0.94	0.85	0.60	0.94	0.90	0.97
CV(in situ)	0.94	-0.35	0.94	0.81	0.55	0.93	0.91	0.97
Shrinkage	0.21	0.04	0.12	0.08	0.04	0.12	0.07	0.13
BAD (core)	0.96	-0.27	0.95	0.82	0.56	0.92	0.91	0.97
ER	-0.90	0.35	-0.90	-0.84	-0.62	-0.95	-0.85	-0.94
Air perm.	-0.85	0.11	-0.82	-0.80	-0.61	-0.86	-0.77	-0.86
CO_2 loss	-0.62	-0.13	-0.65	-0.19	0.13	-0.37	-0.70	-0.58
CO_2 dust	-0.83	0.26	-0.82	-0.61	-0.34	-0.78	-0.80	-0.84
CO_2 res.	0.86	-0.29	0.87	0.57	0.26	0.75	0.86	0.86
Air loss	-0.36	0.26	-0.23	-0.48	-0.52	-0.42	-0.16	-0.30
Air dust	-0.95	0.26	-0.96	-0.69	-0.38	-0.83	-0.91	-0.94
Air res.	0.88	-0.36	0.83	0.78	0.57	0.85	0.76	0.86
Crush st.	0.80	-0.36	0.78	0.43	0.13	0.63	0.74	0.76
Crush elec.	0.55	-0.45	0.52	0.28	0.08	0.47	0.44	0.52
Flex. st.	0.73	-0.30	0.78	0.77	0.59	0.82	0.77	0.81
Frac. st.	0.54	-0.65	0.57	0.06	-0.25	0.27	0.50	0.48
True dens.	-0.06	0.28	-0.12	0.09	0.20	0.07	-0.13	-0.06
CTE	0.56	-0.47	0.51	-0.06	-0.38	0.18	0.49	0.41
Th. Cond.	0.67	-0.44	0.63	0.80	0.71	0.86	0.57	0.73

Table J-2: Correlation between pitch properties and anode properties (%CT: percentage of coal-derived material, see Section 1.5 and Table 6-3 for abbreviations).